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Investigation of New Solar Regenerative Fuel Cell Systems

FINAL REPORT FOR PERIOD 15 MARCH 1961 TO 14 MARCH 1962

CONTRACT DA 36-039 SC-87425 EOS REPORT 1720-FINAL 24 MARCH 1962

PREPARED FOR COMMANDING OFFICER

U.S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY, FORT MONMOUTH, N.J.

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ELECTRO-OPTICAL SYSTEMS, INC., Pasadena, California

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Final Progress Report

INVESTIGATION OF NEW SOLAR REGENERATIVE FUEL
CELL SYSTEMS

Prepared for

Commanding Officer
U.S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY

Contract DA 36-039 SC-87425

15 March 1961 - 14 March 1962

EOS Report 1720-Final

24 March 1962

The work performed in this contract was made possible
by the support of ARPA under Order No. 80-61 through
the U.S. Army Signal Research and Development Laboratory.

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PURPOSE

The purpose of contract DA 36-039-87425 was to perform an analytical evaluation of photochemical energy conversion and thermal energy conversion, where the latter is accomplished by thermally regenerative fuel cells. A very limited amount of development of one specific thermally regenerative fuel cell, the sulfuric acid concentration cell, was also performed.

Solar energy conversion is examined from the standpoint of fuel cells regenerated either photochemically or thermally. The conclusion is reached that very few photochemical reactions known at present are suitable for solar energy conversion. An exception appears to be reactions based on the photo-dissociation of iodine.

A set of criteria is suggested for evaluating chemical systems for use in thermally regenerative fuel cells, and some of these criteria are then applied to several classes of compounds. The theoretical maximum efficiencies are determined by the temperature limits and heat capacities. By this criterion alone it would appear that a large number of chemical systems would be suitable for thermal energy conversion, but the application of the other criteria eliminate most of these from consideration.

A kinetics analysis indicates that for most systems dissociator reaction rates should offer no difficulties, but in the absence of more experimental data no conclusions are drawn concerning electrochemical rates.

PUBLICATIONS, REPORTS, AND CONFERENCES

a. Publications

F.A. Ludwig, D.H. McClelland, and H.A. Frank, "Design Parameters for Regenerative Cells," presented at 15th Annual Power Sources Conference, 9 May 1961, Atlantic City, New Jersey.

b. Reports

The monthly and semi-annual reports to the Signal Corps constituted the only reports on the work of the present contract.

c. Conferences

1. On 7 April 1961, Mr. Frank A. Ludwig of Electro-Optical Systems, Inc. met with Mr. David Linden and Dr. Herbert Hunger of the Signal Corps at Fort Monmouth, New Jersey. It was concluded that the work should be changed from a partly theoretical, partly experimental program to a completely theoretical program.
2. On 15 November 1961 Mr. Gabriel DiMasi of the Signal Corps met with Mr. Charles Stephens and Mr. John J. Rowlette of Electro-Optical Systems at Electro-Optical Systems, Inc. in Pasadena, California. It was concluded that the thermodynamic analysis should be terminated as soon as possible in order to work on the kinetics analysis.

1. INTRODUCTION

An analysis was made of the maximum energy conversion efficiency theoretically obtainable from photochemical processes. A similar analysis was made of thermochemical systems for use in thermo-galvanic converters, and finally a comparison between the two energy conversion methods was made in which efficiency and other important aspects of a functioning converter were considered. The report includes a short comparison between thermally regenerative fuel cells and other thermal energy converters in addition to the other analyses. The report also contains the results of a very limited amount of experimental work done on the sulfuric acid concentration cell converter.

For the photochemical systems, a survey was made of all endothermic photochemical reactions which have been studied and which show any promise of converting solar energy in a practical manner. Of the thirty reactions covered by this analysis, it is shown that only a few of these can ever hope to be the basis of a practical photochemical converter.

Two sets of analyses were made for the reactions. For the first set, which is summarized in Table I, values of E_{\max} are calculated on the basis of experimental values of wavelengths of light and of quantum yields. E_{\max} is the maximum efficiency obtainable for a given reaction and given wavelength when using solar energy, and is the product of two factors. One factor, ϵ_{\max} , refers to the maximum efficiency for any reaction when using sunlight. It is a function only of the solar energy distribution curve and tells nothing about any particular photochemical reaction. The other factor, Q' , is Calvert's definition of maximum efficiency for a given photochemical reaction. Calvert's definition is a function of chemical properties associated with the reaction and refers to no particular light source, but instead to monochromatic light of a particular wavelength.

The second set of analyses is summarized in Table II of Sec. 2.6. This table is made up in part from a few of the better reactions in the first set of analyses, and in part from some other promising reactions for which insufficient experimental data were available for their inclusion in the first set. The basis on which the latter analyses were made differs from that of the earlier analyses in that values of λ_{max} , the maximum possible wavelength which can initiate the primary reaction, have replaced λ . (Values of λ_{max} were also included in the first table but the calculated values of ϵ_{max} , etc., were not based on them.) The values of E'_{max} based on λ_{max} are significant as they show the absolute maximum possible efficiency for a given reaction when using sunlight. That is, it takes into account the possibility of using photosensitizers and anything else necessary to achieve perfect quantum efficiency right up to the wavelength λ_{max} .

Since the photolysis of water has long been of interest as a method of converting solar energy, in part because of its obvious application to hydrogen-oxygen fuel cells, a summary of the different methods for accomplishing this is given in Sec. 2.4. Not all paths outlined here have been studied to date, but the ones which have been studied are pointed out. The goal of the photochemical analyses has been to set maximum efficiency limits, but in some of the methods of water photolysis insufficient data are available to do this.

The Hill reaction is very briefly discussed and analyzed in Sec. 2.5. It is concluded that this reaction definitely can represent energy conversion, but with very low efficiency.

In Sec. 2.7, a short analysis is given concerning the maximum current densities which a certain class of photochemical converters would experience, and qualitatively what effect this current density would have on efficiency.

A conclusion was drawn in EOS Report 420-Final that a condition for Carnot efficiency for a thermally regenerative fuel cell is $\Delta C_p = 0$. That $\Delta C_p = 0$ is a condition for Carnot efficiency has more recently

been disputed by J.B. Friauf, who gives a somewhat different expression for the necessary condition. In the present report a re-evaluation of our original position has been made and it is shown that Friauf's expression reduces, in several important special cases, to $\Delta C_p = 0$. Two apparent paradoxes from EOS Report 420-Final are also explained.

In Sec. 3.3 a re-examination of criteria for a practical thermally regenerative fuel cell has been made. It is shown first that there is no single criterion by which to evaluate the chemical systems for thermally regenerative fuel cells. Five criteria have been set up and are used for predicting the merits of specific chemical systems.

A survey of binary (two element) compounds was made under the previous contract, DA-36-039-SC-85270, in which enthalpy and free energy data were summarized, and certain other thermodynamic properties were tabulated in a few cases. In this report an extension of that work has been made to include tertiary compounds. Several binary compounds which do not decompose to the elements, and therefore were not included in the analyses of contract DA-36-039-SC-85270, have been included in this report. A number of organic hydrogenation compounds have also been included, together with a specific method for using them in a thermally regenerative fuel cell.

It is pointed out in Sec. 3.3 that dE/dT , the rate of change of potential with temperature for a reaction, is an important criterion for selecting a reaction for a practical converter. Since this quantity is equal to $\Delta S/n\mathcal{F}$, where n is the number of electrons per reaction and \mathcal{F} is the value of the Faraday, values of $-\Delta S^\circ/n$ were calculated for each compound. Melting points were also included, when available, for the compounds and their dissociation products. This property may also be very important in selecting a chemical system.

A kinetics analysis was made in which both regeneration kinetics and electrode kinetics were considered. For the former, a figure of merit was defined which relates current density in the cell to minimum dissociator volume. It is shown that electrode reaction rates are not determined completely by the chemical system. The general evaluation is therefore less conclusive than that of the regeneration process.

Experimental work done on the sulfuric acid concentration cell converter was limited to the design and construction of the cycling equipment and one polarization curve. This work was terminated at the request of the contracting agency.

Finally, there was a comparison made between thermally regenerative fuel cells and photochemical converters, and another comparison between thermally regenerative fuel cells and other thermal energy converters. Both comparisons considered several practical aspects of some hypothetical systems in addition to theoretical maximum efficiencies.

2. PHOTOCHEMICAL ENERGY CONVERSION

If solar energy conversion is to be accomplished by photochemical reactions in a manner which is competitive with presently available photovoltaic converters, then a search must be made for reactions which have certain indispensable properties. Aside from the obvious property of being endothermic, the most important properties to be optimized are: (1) threshold wavelengths, (2) quantum yields, and (3) absence of thermal degradation reactions. This latter point is to be distinguished from thermal back reactions which lead to a regeneration of all the reactants. It refers, instead, to dismutation reactions and other exothermic processes which are inherent in the course of the over-all photochemical reaction. The second and third properties are expressed by E_{\max} , the maximum possible conversion efficiencies based on experimental values of the quantum yield at a given wavelength. Values of E_{\max} for twenty-five reactions are shown in Table I. In Table II values of E'_{\max} are given for twelve reactions. E'_{\max} is equivalent to E_{\max} except that theoretical threshold wavelength and theoretical maximum quantum yields are assumed. The importance of this somewhat hypothetical concept is that it shows rigorously, within the limits set forth in Sec. 2.1, what the upper limit of conversion efficiency is for a given reaction.

2.1. Maximum Possible Photochemical Efficiency

Although not directly Carnot limited, photochemical converters using sunlight have a limitation just as rigid if certain assumptions are made about the photochemical process. If there exists a definite threshold energy, below which the reaction cannot be initiated, and if only one quantum is involved in each primary process, then it can be shown that there is an optimum wavelength for maximum efficiency (Ref. 1). This arises from the fact that all energy in a quantum in excess of that necessary to promote the primary process will be given off as heat.

The maximum efficiency, ϵ_{\max} , is related to the threshold frequency by

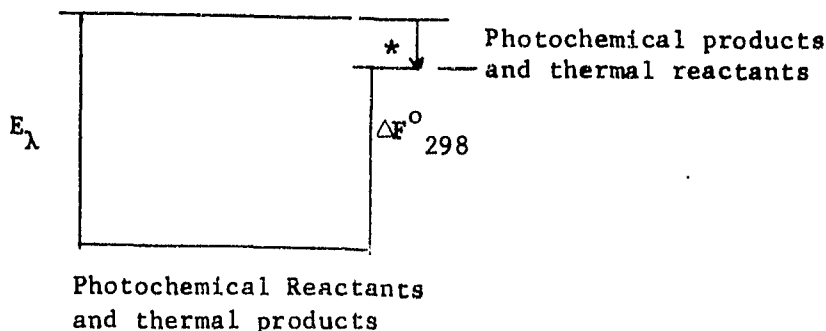
$$\epsilon_{\max} = \frac{h\nu_0 \int_0^{\infty} n(\nu) d\nu}{\int_0^{\infty} n(\nu) h\nu d\nu} \quad (1)$$

Figure 1, which relates ϵ_{\max} to λ , was then plotted in terms of wavelength since photochemical data are generally expressed in those units. This curve is based on the solar energy distribution curve compiled by Johnson, which refers to sunlight outside the earth's atmosphere (Ref. 2). Since the data for the Johnson curve are experimental, the curve in Fig. 1 is also based on experimental measurements.

It has been pointed out by Calvert that the percent efficiency of a photochemical reaction can be given by:

$$Q = 100 (\Delta F_{298}^0)(\phi_A/E_\lambda) \quad (2)$$

where ΔF_{298}^0 is the standard free energy increase for the over-all chemical reaction (i.e., the energy available when the photochemical products return to their initial state), ϕ_A is the quantum yield of the given product A, and E_λ is the energy of the absorbed light of wavelength λ (Ref. 3). In terms of the following diagram:



it is seen that this relation expresses the fact that there is an activation energy (represented by * on the diagram) which is a loss, and the efficiency is given by the ratio of ΔF_{298}^0 to E_λ , multiplied by

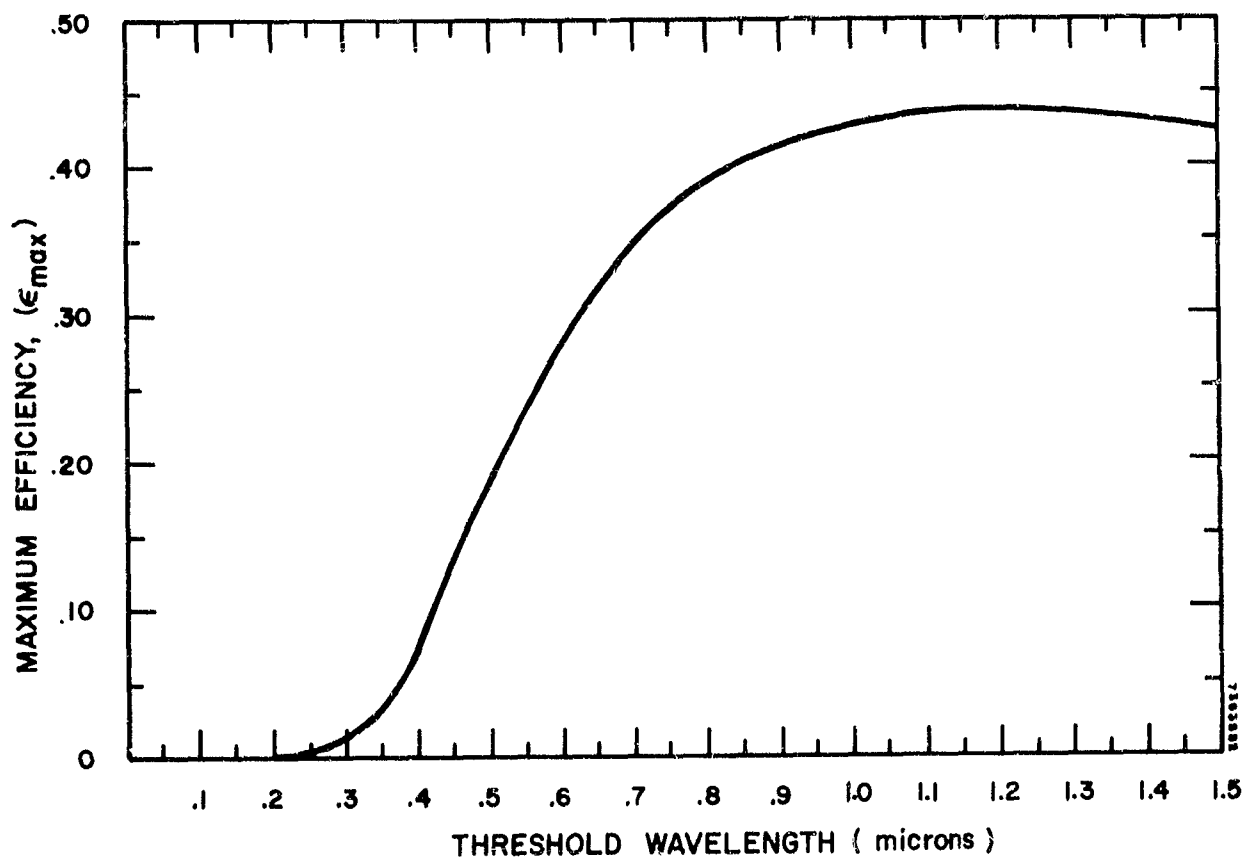


FIG. 1 MAXIMUM EFFICIENCY FOR SOLAR PHOTOCHEMICAL PROCESSES

the quantum yield. This efficiency is, of course, a maximum when Φ_A reaches a value corresponding to no side reactions. The maximum value of Φ_A is usually a simple number like 0.5, 1.0 or 2.0, but determined in any event by the reaction mechanism. The expression can then be combined with that of Trivich and Flinn to yield the following relation:

$$E_{\max} = (Q/100) \epsilon_{\max} = \frac{\Delta F^0}{hc} 298 \Phi_A \lambda_0 \epsilon_{\max} \quad (\text{Ref. 4}) \quad (3)$$

In this equation, λ_0 represents the wavelength of threshold energy and c is the velocity of light, and when used in conjunction with Fig. 1 should prove useful in evaluating new solar photochemical conversion systems and in influencing the direction of new work in that field.

2.2 Endothermic Photochemical Reactions

Table I is a compilation of many of the more important endothermic photochemical reactions which have been studied. All values reported for λ and Φ are experimental and, consequently, the calculated values for Q' and E_{\max} are experimental so far as the photochemical part of the conversion process is concerned. It was pointed out in Sec. 2.1 that ϵ_{\max} is also based on experimental measurements. There are five assumptions made about the hypothetical conversion processes of Table I. They are the following:

- a. The photochemical part of the conversion process occurs by a quantum process in which an absorbed photon initiates the reaction only if its energy is at least equal to the threshold energy. Any excess energy is given off as heat.
- b. The photochemical products are separated from one another and from the reactants.
- c. An electrochemical reaction results in the conversion of this potential chemical energy into electrical energy.
- d. The electrochemical reactants and products are at unit activity.
- e. The assertion has been made previously that it is apparently possible in principle to devise a scheme for converting a few high energy quanta into many low energy quanta with energy still at least equal to the threshold energy (Ref. 4). This possibility is excluded in this analysis.

TABLE I*

MAXIMUM SOLAR ENERGY CONVERSION EFFICIENCIES FOR SOME ENDOTHERMIC PHOTOCHEMICAL REACTIONS

REACTION	λ	λ_{\max}	ϕ	ΔF°_{298}	Q'	ϵ_{\max}	E_{\max}	REFS.
1. $\text{NH}_3 \longrightarrow 1/2 \text{N}_2 + 3/2 \text{H}_2$	2194	2800	0.14 (NH_3)	0.183	4.5×10^{-3}	0.001	4.5×10^{-6}	5
	2200		0.6	0.183	0.020	0.001	2.0×10^{-5}	
	2138		0.25	0.183	9×10^{-3}	<0.001	< 10^{-5}	
2. $\text{HBr} \longrightarrow 1/2 \text{H}_2 + 1/2 \text{Br}_2$	2537	3265	2.0 (HBr)	1.05	0.430	0.004	1.7×10^{-3}	6
3. $\text{HI} \longrightarrow 1/2 \text{H}_2 + 1/2 \text{I}_2$	2820	4085	2.0 (HI)	0.536	0.242	0.006	1.4×10^{-3}	7
4. $\text{H}_2\text{S} \longrightarrow \text{H}_2 + \text{S}$	2050	3175	2 (H_2S)	0.282	0.093	0.001	< 10^{-4}	8
5. $3\text{I}^- + 2 \text{Fe}(\text{CN})_6^{-3} \longrightarrow \text{I}_3^- + 2 \text{Fe}(\text{CN})_6^{-4}$	6300	8030	1.0 (I_3^-)	0.352	0.179	0.308	0.055	9
6. $\text{I}_3^- + 2 \text{Fe}^{++} \longrightarrow 3\text{I}^- + 2 \text{Fe}^{+3}$	5461	8030	1.0 (I_3^-)	0.470	0.207	0.236	0.049	10
7. $\text{NO}_3^- \longrightarrow \text{NO}_2^- + 1/2 \text{O}_2$	2536	-----	0.3 (NO_3^-)	1.610	0.13	0.004	5.2×10^{-4}	11
	2130		0.01	1.610	4×10^{-3}	0.017	6.8×10^{-5}	
7a. $\text{H}^+ + \text{NO}_3^- \longrightarrow \text{HNO}_2 + 1/2 \text{O}_2$	2536		0.05 (NO_3^-)	0.22	2×10^{-3}	0.005	8×10^{-6}	
8. $\text{NO}_2 \longrightarrow \text{NO} + 1/2 \text{O}_2$	4050	3930	0.5 (NO_2)	0.392	0.061	0.084	5.1×10^{-3}	12
	3660		1.83	0.392	0.212	0.050	0.0106	
	3130		1.93	0.392	0.190	0.017	3.2×10^{-3}	
9. $\text{N}_2\text{O}_4 \longrightarrow 2\text{NO} + \text{O}_2$	2650	-----	0.4 (N_2O_4)	0.784	0.067	0.004	2.7×10^{-4}	13
10. $\text{NOCl} \longrightarrow \text{NO} + 1/2 \text{Cl}_2$	6370	7605	2.0 (NOCl)	0.2108	0.2168	0.312	0.0676	14
11. $3\text{O}_2 \longrightarrow 2\text{O}_3$	2000	2395	1.3-2.0 (O_2)	3.36	1.14	<0.001	< 10^{-3}	15
	1750		2.0	3.36	0.948	<0.001	< 10^{-3}	16
12. $\text{SO}_3 \longrightarrow \text{SO}_2 + 1/2 \text{O}_2$	2760	3460	0.35 (SO_3)	2.06	0.161	0.005	8.0×10^{-4}	17

*Column headings and their units are defined in text on pages 11 and 12.

TABLE I (cont)
MAXIMUM SOLAR ENERGY CONVERSION EFFICIENCIES FOR SOME ENDOTHERMIC PHOTOCHEMICAL REACTIONS

REACTION	λ	λ_{\max}	ϕ	ΔF°_{298}	Q'	ϵ_{\max}	E_{\max}	REFS.
13. $\text{COCl}_2 \longrightarrow \text{CO} + \text{Cl}_2$	2750	----	0.9(COCl_2)	0.707	0.14	0.005	7×10^{-4}	18
14. $\text{I}_3^- + \text{H}_2\text{O} + \text{HNO}_2 \longrightarrow 3\text{H}^+ + \text{NO}_3^- + 3\text{I}^-$	4360	8030	0.1(I_3^-)	0.82	0.029	0.115	3.3×10^{-3}	19
15. $\text{Fe}^{++} + \text{H}_2\text{O} \longrightarrow 1/2 \text{H}_2 + \text{Fe}^{+3} + \text{OH}^-$	2900	2850	0.05(Fe^{++})	1.185	0.014	0.008	1.1×10^{-4}	20
16. $\text{Fe}^{++} + \text{H}^+ \longrightarrow 1/2 \text{H}_2 + \text{Fe}^{+3}$	2537	2850	0.1(Fe^{++})	0.771	0.0156	0.004	6.2×10^{-6}	21
17. 2 anthracene \longrightarrow dianthracene	3660	----	0.25(dian.)	0.68	0.050	0.050	2.5×10^{-3}	22
18. $\text{AgCl} \longrightarrow \text{Ag} + 1/2 \text{Cl}_2$	4050	4830	1.0(AgCl)	1.136	0.371	0.084	0.031	23, 24
19. $\text{AgCl} + 1/2 \text{H}_2\text{O} \longrightarrow \text{Ag} + \text{H}^+ + \text{Cl}^-$ $+ 1/4 \text{O}_2$	4050	4830	1.0(AgCl)	1.007	0.329	0.084	0.028	25, 26
20. $\text{AgBr} \longrightarrow \text{Ag} + 1/2 \text{Br}_2$	4600	5660	1.0(AgBr)	0.955	0.344	0.144	0.0495	27
21. $\text{AgI} \longrightarrow \text{Ag} + 1/2 \text{I}_2$	4400	7105	1.0(AgI)	0.689	0.244	0.120	0.0294	28
22. $\text{H}_2\text{O} + 1/2 \text{O}_2 \longrightarrow \text{H}_2\text{O}_2$	3660	----	0.09(H_2O_2)	2.18	0.058	0.050	2.9×10^{-3}	29
23. $\text{H}_2\text{O} \longrightarrow \text{H}_2 + 1/2 \text{O}_2$	1650	2385	0.3(H_2O)	2.458	0.098	$<< 0.001$	$<< 10^{-4}$	30
24. $\text{Ce}^{+3} + \text{H}_2\text{O} \longrightarrow \text{Ce}^{+4} + 1/2 \text{H}_2 + \text{OH}^-$	2537	~ 2600	0.0013(Ce^{+3})	1.20	3.2×10^{-4}	0.004	1.3×10^{-6}	31
25. Thionine + $\text{Fe}^{++} \longrightarrow$ Leucothionine + Fe^{+3}	> 5790	----	-----	----	-----	0.28	$< 0.22^*$	32

*See page 15 (bottom of page)

The E_{\max} values in Table I show that all but a few could not lead to efficiencies of even one percent. Several reactions which show very small ultimate potential were included in the table because they have been studied in recent years from the standpoint of possible solar energy conversion. Several others were included because they are good examples to illustrate various types of inefficiencies which can arise.

A number of additional comments about Table I are in order. First, Calvert's efficiency Q has been replaced by $Q' = Q/100$ (Ref. 3).¹ Second, ΔF_{298}° is given in electron volts per molecule multiplied by the number of electrons per reaction.

The quantity E_{\max} is then given by

$$E_{\max} = Q' \epsilon_{\max} = \frac{\Delta F_{298}^{\circ} \phi \lambda}{12,395} \epsilon_{\max} \quad (4)$$

where λ is expressed in \AA and ϵ_{\max} is given by Eq. 1.

These units were considered more convenient for use here than kcal/mole, since in almost every case the only practical method of operating an electrochemical cell with the reaction in question would be in aqueous solution and these values are compiled in tables of oxidation-reduction potentials. However, in many cases the photochemical reactions were carried out in the gas phase. Since Q' (and therefore E_{\max}) was calculated on the basis of gas phase photochemical reactions and electrochemical reactions in aqueous solution, the values for Q' differ (in addition to the factor of 100) from the corresponding ones of Calvert in some cases. It is felt that the calculations made for Table I are more significant because in several cases it seems likely that the photochemical reactions would be in the gas phase, while in almost all cases the electrochemical cells would operate in aqueous solution. Thermal energy would, of course, be necessary to vaporize the material for photolysis but there should never be any dearth of heat in the system. This does mean,

1. Calvert's definition of efficiency refers to monochromatic light of wavelength equal to that used in obtaining the experimental quantum yields.

however, that the converters would not be purely photochemical. In general, this increases the magnitude of Q' due to hydration energy, and in one case (reaction 11 at 2000 Å) $Q' > 1$.

Under the column headed λ_{\max} are listed the maximum wavelengths with energy sufficient to initiate the primary photochemical reaction, but it should be born in mind that the calculated values of ϵ_{\max} , E_{\max} , etc., are based on λ , the experimental wavelengths. In a few cases, this primary process was unknown, or else the energy requirement for it was unknown. It is interesting that in two reactions, numbers 8 and 15, the reactions were reported with slightly less than the theoretical minimum energy.

In parentheses, following the value of Φ , is the chemical species on which Φ is based. In every case, except for reactions 22 and 23, this is also the absorbing species. Mercury vapor was used as the photosensitizer in 22, and zinc oxide in 23.

2.3 Evaluation of Photochemical Reactions

The endothermic reactions of Table I will now be evaluated from the standpoint of solar energy conversion. In Sec. 2.6 some of the better ones will be evaluated on a somewhat hypothetical basis.

Reactions 1, 2, 3, 4, 7, 9, 11, 12, 13, 15, 16, 23, and 24 have all been carried out only by using wavelengths of less than 3500 Å. At this wavelength ϵ_{\max} is only by about 0.04, and an over-all conversion efficiency of more than 2 or 3 percent could not be reasonably hoped for. It can further be seen by the values of λ_{\max} that none of these can be carried out at wavelengths significantly longer than 3500 Å, even with photosensitizers.

Numbers 1 and 4 also look very unattractive because electrochemical reactions utilizing the photochemical products look almost impossible. In reactions 8 and 9 it appears very doubtful that oxygen could be separated from nitric oxide before recombination.

Number 24, the photoreduction of water by cerous ion, is one of a large number of possible reactions to accomplish either the photoreduction or the photooxidation of water. These photochemical reactions are characterized by electron transitions either to or from the central

species (such as Ce^{+3}). Marcus refers to them, respectively, as reductive and oxidative cases of electron transfer (Ref. 33). In aqueous solution the electron is transferred either from or to a water molecule which results in either the oxidation or the reduction of water. Although, from the standpoint of solar energy conversion, reaction 24 is certainly not practical and can never be in view of the wavelength for the electron transfer,¹ there are other species which cannot be so easily ruled out. Two of these reactions will be briefly discussed in Sec. 2.6.

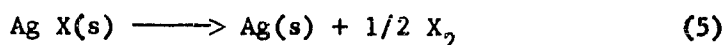
The quantum yield shown in the table for number 22, the photosynthesis of hydrogen peroxide, is misleading as it is questionable whether hydrogen peroxide has ever been made by an endothermic photochemical reaction. Even with zinc oxide as the photocatalyst the reactions have usually been carried out in the presence of organic additives such as sodium formate or phenol. These additives are reducing agents which enter into the stoichiometric reaction with the result that the over-all reactions are exothermic (Refs. 4, 34, and 35). Even when zinc oxide is used alone it appears to enter into the reactions in such a way that the over-all process becomes exothermic (Ref. 36). When cadmium sulfide is used in place of zinc oxide it very definitely enters into the reaction. In fact, the oxidation of the sulfide to the sulfate is then the main reaction, with the result that again the over-all reaction is exothermic (Ref. 37). With cadmium telluride the reaction is apparently endothermic but the quantum yields are very low. Recently, in this laboratory, the photosynthesis of hydrogen peroxide was accomplished in such a manner that the reactions were apparently endothermic although this was not definitely proven (Ref. 4). These were gas phase reactions photosensitized on solid surfaces ($\text{ZnO-Ag}_2\text{O}$ and CdTe) in a flow system. A value of λ_{max} for this reaction was not put in the table as the minimum energy

1. L.J. Heidt reports the photolysis of water in the cerous-ceric perchlorate system at wavelengths as long as 3500 \AA , although with infinitesimal quantum yields (Ref. 31). However, the absorption spectrum which he gives for cerous perchlorate indicates the electron transfer begins at about 2600 \AA , extending to shorter wavelengths.

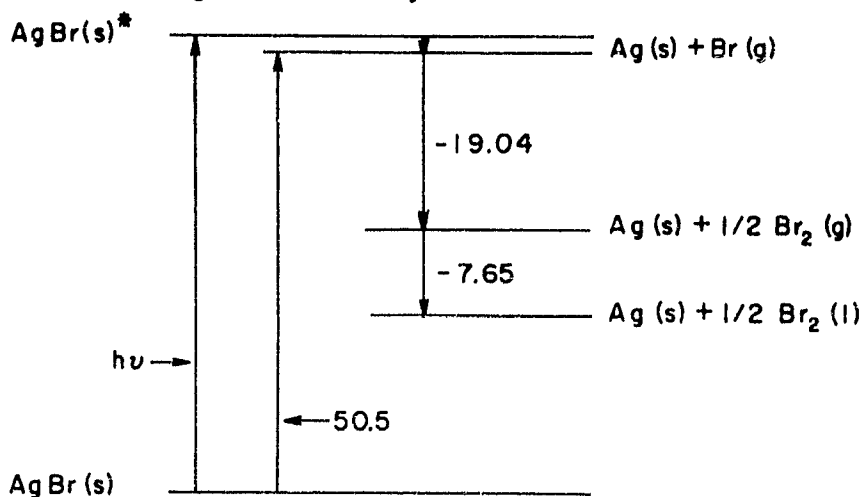
for the reaction is not known. Calvert has set up a model for the photosynthesis of hydrogen peroxide in which a solid semiconductor is used as a photosensitizer (Ref. 37). However, it is not clear whether or not the threshold wavelength is the one just necessary for the creation of an electron-hole pair in the semiconductor.

Number 17, the dimerization of anthracene, is one more reaction that can be reasonably ruled out for solar energy conversion. Apparently, ultraviolet light is necessary for this reaction and, in addition, the dimerization takes place in an organic solution, which would make the electrochemical utilization of this converted energy quite difficult, or even impossible.

The silver halide reactions (18, 19, 20, and 21 in Table I) require a somewhat more detailed analysis as the threshold wavelengths appear surprisingly short. The values for λ_{\max} were calculated on the basis of the enthalpy for the following reaction:



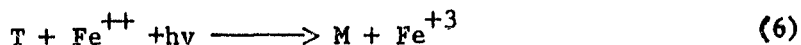
where X_2 was gaseous, liquid, or solid for chlorine, bromine, or iodine respectively. For AgBr $\lambda_{\max} = 5660 \text{ \AA}$ although it is well known that AgBr can be used in the photographic process well into the infrared (at least to $13,000 \text{ \AA}$) by use of photosensitizers. The question presented, then, is to explain how photosensitizers, which cannot affect λ_{\max} , can enable silver to be deposited at wavelengths longer than 5660 \AA . In terms of the following Born-Haber cycle



it can be seen that the energy necessary to promote an electron to the conduction band is at least equal to the energy of formation of crystalline silver bromide from silver and atomic bromine. The values indicated are in kcal/mole for the various steps. In this diagram AgBr(s)^* represents solid silver bromide with an electron excited to the conduction band. It is not meant to be implied by the diagram that $h\nu > 50.5$ kcal, but that it is at least equal to that much.

When an organic dye is used as a photosensitizer to extend the wavelength of sensitivity, the energy for electron transfer either to a silver ion or unoccupied hole in the conduction band will have to be less than for the creation of a halogen atom. Less than the stoichiometric amount of halogen will have been produced and the conditions for a photochemically regenerative cell described by reactions 18 through 21 in Table I will not have been met. A similar situation is met when a small amount of cuprous ion replaces an equal amount of silver ion in the lattice. It is much easier to raise an electron from the cuprous ion to the conduction band than to raise an electron from bromide ion, and in practice it is found that the bromine production is considerably less than the stoichiometric amount required in reaction 20 (Ref. 38). Therefore, it must be concluded that the values of ϵ_{max} listed in Table I for these reactions really do represent maximum efficiencies. The silver halide reactions are of interest inasmuch as they have been studied in recent years as possible solar energy converters, and only recently a functioning silver bromide photocell was described in the literature (Ref. 39).

Reaction 25 also requires some additional explanation. Following the absorption of light, thionine becomes capable of oxidizing ferrous ion to ferric. The value of λ_{max} is apparently not known as yet, but wavelengths as long as 5790 \AA are known to be effective (Ref. 40). The thionine is reduced to mesothionine which dismutates to give thionine and leucothionine according to the following scheme in which T represents thionine, L represents leucothionine, and M represents mesothionine:



Equation 6 is the net reaction for the photochemical part and Eq. 7 is the net reaction for the disproportionation. The significant point which is brought out by these equations is that the maximum value for Φ is 0.5. Although E_{\max} based on λ_{\max} cannot be calculated until this latter quantity is known, the limits of E_{\max} can be calculated from the knowledge that $\lambda_{\max} \geq 5790 \text{ \AA}$ (where $\epsilon_{\max} = 0.28$) and that the maximum value for $\epsilon_{\max} = 0.44$ at $12,000 \text{ \AA}$ for any reaction. Since $\Phi_{\max} = 0.5$ it can be seen that $0.14 \leq E_{\max} \leq 0.22$, where E_{\max} is the hypothetical value based on Φ having its maximum value of 0.5. The actual limits would have to be placed below these on account of the dismutation reaction. Since this reaction is exothermic, there is an additional energy degradation.

Some early experiments made by Rabinowitch generated considerable interest in this particular system (Ref. 41). By dipping inert electrodes into two solutions of ferrous ion and thionine, one electrode illuminated and the other kept in the dark, he observed a potential of about 0.5 volt. Because of the rapidity of the reverse reaction, however, actual quantum yields do not approach the theoretical value, with the result that currents are quite low. The similarity between this system and the iodine-iron system described in Sec. 2.6 of the present report should be quite evident. But with the iodine-iron system there is no energy degradation process analogous to Eq. 7 so that $\Phi_{\max} = 1.0$. In addition, experimental values of Φ have been approximately 1.0 at all wavelengths thus far investigated.

2.4 Processes for Water Photolysis

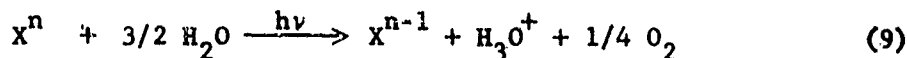
Only the direct photolysis was considered in Table I and the theoretical maximum wavelength for this was shown to be 2385 \AA , although there have been reports of dissociation with very low yield at 2537 \AA , sensitized with mercury vapor (Refs. 42, 43, 44, and 45). In view of the relatively high stage of development of hydrogen-oxygen fuel cells it would be very desirable to have photochemical regeneration of these

cells. For that reason a somewhat more detailed look at possible methods for accomplishing this will now be considered. The various possibilities can be broken down in the following manner.

I. Direct photolysis to give hydrogen and oxygen

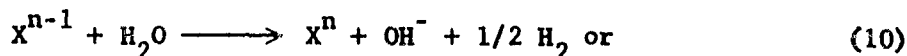


II. Endothermic photochemical reduction of photocatalyst with production of oxygen

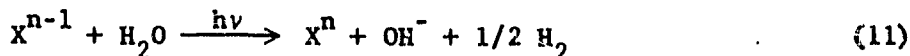


followed by,

a. Thermal reduction of water to give hydrogen

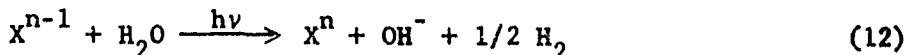


b. Photochemical oxidation of reduced photocatalyst to give hydrogen



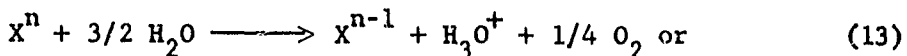
III. Exothermic photochemical reduction of photocatalyst with production of oxygen followed by path b. of reaction II.

IV. Endothermic photochemical oxidation of photocatalyst with production of hydrogen

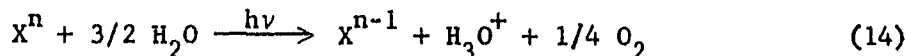


followed by,

a. Thermal oxidation of water to give oxygen,



b. Photochemical reduction of oxidized photocatalyst to give oxygen



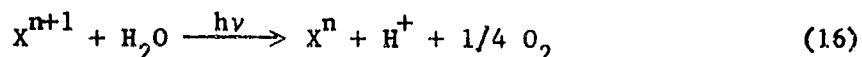
V. Exothermic photochemical oxidation of photocatalyst with production of hydrogen followed by path b. of reaction IV.

VI. Endothermic or exothermic photochemical electron transfer from photocatalyst to electron acceptor,



followed by

a. Thermal oxidation of water to oxygen by the photocatalyst



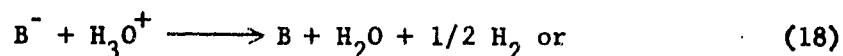
b. Endothermic electron transfer to second electron acceptor from first electron acceptor



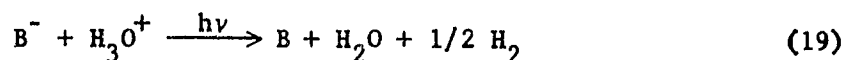
and

c. Production of hydrogen by

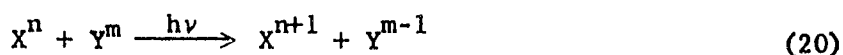
1. Thermal reduction of water by reduced form of second electron acceptor



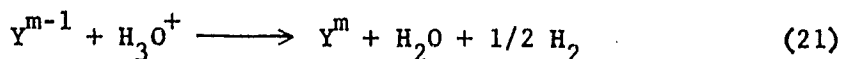
2. Photochemical oxidation of second electron acceptor



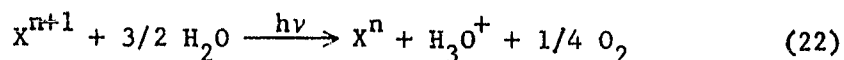
VII. Photochemical endothermic electron transfer from photocatalyst 1 to photocatalyst 2.



with thermal reduction of water to hydrogen by reduced form of photocatalyst 2,



followed by photochemical reduction of oxidized form of photocatalyst 1 with production of oxygen



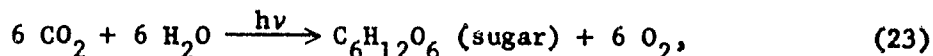
Several possible processes are not included since they are highly unlikely of realization or even impossible. Thus III a and V a were not considered since they would imply a substance whose reduced form could thermally reduce water and whose oxidized form could thermally oxidize water.

Process V is identical to II b except that the photocatalyst oxidation is light catalyzed.

A number of inorganic ions in solution are known which have electron transfer spectra indicating they may be capable of accomplishing the initial steps in reactions II and IV (Ref. 33). The spectra of all photocatalysts for process IV are in the ultraviolet, and hence would lead to an unacceptable value of E_{\max} , and with very few exceptions the same is true for those of process II. One of these exceptions has previously been treated.¹

Process III describes the ceric-cerous system investigated so thoroughly by L. J. Heidt, which has also been previously treated.² Note that these reactions could also proceed by process IV b, that is, endothermic photochemical oxidation of the photocatalyst with production of hydrogen followed by thermal oxidation of water to give oxygen.

The significance of process VI is that it is analogous to the natural photosynthesis reaction except that the decomposition of water is accomplished. The photosynthesis reaction, which can be represented by



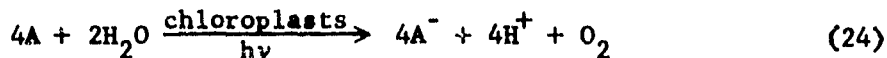
is considerably more endergonic than is the decomposition of water, yet can be carried out with red light. For each mole of water reacted the former is endergonic to the extent of 112 kcal., and the latter about 68 kcal. The photosynthesis process in nature can be accomplished

-
1. Reaction 29 of Table I
 2. Reaction 24 of Table I

with low energy radiation because of the additivity of energies in the several light absorption steps. The reaction can be brought about by wavelengths with energy such that at least four quanta per reaction are necessary, instead of only two as indicated in the hypothetical case of process VI.

2.5 The Hill Reaction

An important reaction was discovered by Hill which has some of the features of the photosynthetic process in nature (Ref. 46). In the Hill reaction, energy conversion may be accomplished by the partial photolysis of water in the presence of chloroplasts and a Hill reaction oxidant, or electron acceptor. The contention of Marcus, Hatchett, and Sancier that "no useful energy is stored in the course of the Hill reaction" is clearly incorrect (Ref. 47). The general process for the net reaction may be written



Now if, for example, A is ferricyanide, then this process is endergonic since oxygen has the potential to oxidize ferrocyanide and regenerate the reactants.

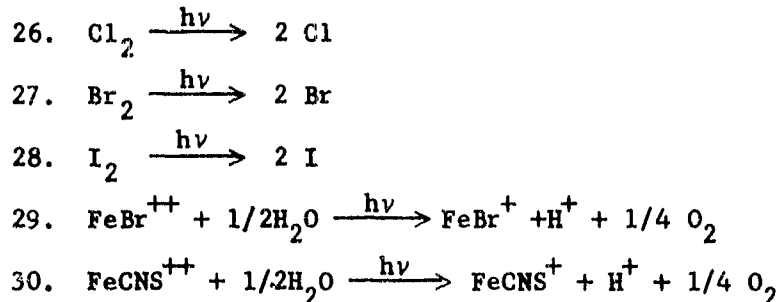
It has been discovered that many complex inorganic ions and quinones are good Hill reaction oxidants, but only if they have absorption bands around 4200-4300 Å, which corresponds to one of the absorption peaks of chlorophyll-a (Ref. 47). This observation can be explained qualitatively in terms of the Frank-Condon principle which requires an overlap of energy levels of reactants for either electron transfer or transfer of electronic excitation energy to occur. But possibly the most pertinent observation is the fact that, like photosynthesis, the Hill reaction can proceed in red light, even though the electron acceptor is sensitive only in the blue. This necessitates at least two quanta per reaction and therefore represents one of two possible ways of getting around the limitations expressed by E_{max} . For the case cited above, in which ferricyanide ion is the Hill reaction oxidant,

light of 6500 Å (1.9 ev) wavelength suffices to bring about the reaction when the absorption band of ferricyanide lies at 4200 Å (2.95 ev). Even though more than one quantum per reaction has been utilized, the Hill reaction does not appear to offer the possibility of an efficient method for the conversion of solar energy. The energy equivalent of 6500 Å is 1.9 ev and two quanta, or 3.8 ev total, are needed. But the standard free energy change is only 0.87 volt. This leads to a value of Q'_{\max} of only 0.23. This small value of Q'_{\max} is due in part to the energy loss in the formation of the oxygen molecule. E_{\max} cannot be calculated from Q'_{\max} and Fig. 1 because E_{\max} is based on the assumption of only one photon per reaction and also that all wavelengths shorter than the threshold wavelength are equally effective. If only light of energy corresponding to the absorption bands of chlorophyll is effective, then the maximum efficiency of the Hill reaction is even less.

The conclusions are that the Hill reaction definitely can represent energy conversion, but only with low efficiency.

2.6 Most Promising Photochemical Reactions

From experimental values of quantum yields at known wavelengths, it is seen from Table I that reactions 5, 6, 10, 18, 19, 20, and 21 are all capable of solar energy conversion with efficiencies of at least 2.8 percent. As pointed out in Sec. 2.2, it is assumed that the photochemical products can be separated and made to react at unit activity in an electrochemical cell to produce an electric current and regenerate the photochemical reactants. It will now be of interest to consider these reactions, together with number 3 since it can potentially give efficiencies of more than a percent, from the standpoint of their potential if perfect quantum efficiency is attained at all wavelengths up to and including the threshold wavelengths. In the present evaluation the restriction of unit activity of electrochemical reactants will not be imposed. In addition to 3, 5, 6, 10, 18, 19, 20, and 21, the following reactions will also be considered:



It will be seen from Table II that reactions 26, 27, and 28 above (Ref. 45) (especially number 28) appear to be especially suited to the conversion of solar energy, if only a way of utilizing the energy of the halogen-halogen bond can be found. A moment's reflection will show that reactions 5 and 6 can do just that if a system is looked at in which the reactants (for number 6) are Fe^{++} and Fe^{+3} at the electrodes.

The potential for the reaction



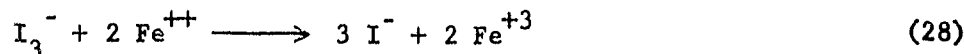
is given by the Nernst equation to be

$$E = E^0 - \frac{RT}{nF} \ln \frac{(\text{Fe}^{+3})}{(\text{Fe}^{++})} = E^0 - 0.06 \log (\text{Fe}^{+3})/(\text{Fe}^{++}) \quad (26)$$

and if the $(\text{I}_3^-)/(\text{I}^-)$ ratio is unity at the two electrodes, then the potential for the cell reaction is

$$E = 0.06 \log \frac{(\text{Fe}^{+3})_l/(\text{Fe}^{++})_l}{(\text{Fe}^{+3})_d/(\text{Fe}^{++})_d} \quad (27)$$

where l and d stand for light and dark, respectively. The $(\text{I}_3^-)/(\text{I}^-)$ ratio can be made approximately unity by having a large excess of the two iodine species as compared to the iron species. For example, if the initial ferrous ion concentration is 0.1 M, and the iodide and triiodide concentrations are each 1 M, then it can be seen from the reaction



that even if all Fe^{++} is oxidized to Fe^{+3} , the $(\text{I}_3^-)/(\text{I}^-)$ ratio will be 0.826 at the illuminated side. The complete expression for the cell potential would, of course, be

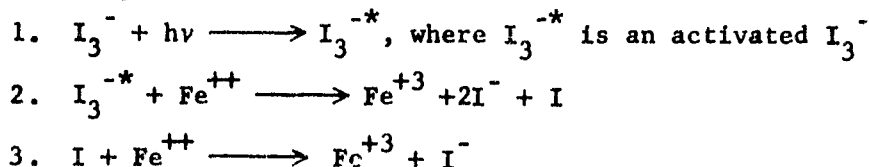
TABLE II*
MAXIMUM POSSIBLE CONVERSION EFFICIENCIES FOR THEORETICAL THRESHOLD WAVELENGTHS

Reaction	λ_{\max}	ΔF_{\max}	Q'_{\max}	ϵ_{\max}	E'_{\max}
3. $\text{HI} \longrightarrow 1/2\text{H}_2 + 1/2\text{I}_2$	4085	1.072	0.354	0.086	0.0304
5. $3\text{I}^- + 2\text{Fe}(\text{CN})_6^{3-} \longrightarrow \text{I}_3^- + 2\text{Fe}(\text{CN})_6^{4-}$	8030	1.542	1.00	0.395	0.395
6. $\text{I}_3^- + 2\text{Fe}^{++} \longrightarrow 3\text{I}^- + 2\text{Fe}^{+3}$	8030	1.542	1.00	0.395	0.395
10. $\text{NOCl} \longrightarrow \text{NO} + 1/2\text{Cl}_2$	7605	0.2108	0.2583	0.380	0.0981
18. $\text{AgCl} \longrightarrow \text{Ag} + 1/2\text{Cl}_2$	4830	1.136	0.444	0.172	0.0763
19. $\text{AgCl} + 1/2\text{H}_2\text{O} \longrightarrow \text{Ag} + \text{H}^+ + \text{Cl}^- + 1/4\text{O}_2$	4830	1.007	0.392	0.172	0.0674
20. $\text{AgBr} \longrightarrow \text{Ag} + 1/2\text{Br}_2$	5660	0.971	0.443	0.257	0.114
21. $\text{AgI} \longrightarrow \text{Ag} + 1/2\text{I}_2$	7105	0.688	0.395	0.358	0.141
26. $\text{Cl}_2 \longrightarrow 2\text{Cl}$	4970	2.493	1.00	0.187	0.187
27. $\text{Br}_2 \longrightarrow 2\text{Br}$	4350	2.319	1.00	0.226	0.226
28. $\text{I}_2 \longrightarrow 2\text{I}$	8030	1.542	1.00	0.395	0.395
30. $\text{FeCNS}^{++} + 1/2\text{H}_2\text{O} \longrightarrow \text{FeCNS}^+ + \text{H}^+ + 1/4\text{O}_2$	~4600	2.70	0.208	0.145	0.030

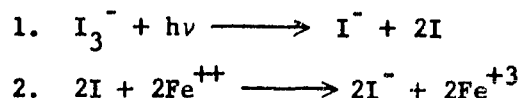
*The max subscripts refer to the maximum possible values of λ , ΔF , Q' , ϵ , and E' which were defined on pages 11 and 12.

$$E = 0.03 \log \frac{(I^-)_\ell (Fe^{+3})_\ell^2 (I_3^-)_d (Fe^{++})_d^2}{(I_3^-)_\ell (Fe^{++})_\ell^2 (I^-)_d (Fe^{+3})_d^2} \quad (29)$$

Since in the actual operation of such a cell the continuous operation will be dependent upon the photochemical production of Fe^{+3} at the light electrode and the thermal production of Fe^{++} at the dark electrode, it will be very important to understand the mechanism for each in order to evaluate this possible photochemical conversion process. The two following mechanisms have been postulated for the photochemical reaction (Ref. 10):



or



In the operation of a photochemical converter based on this reaction, separation of the photochemical products would be unnecessary providing that the thermal reaction can proceed rapidly in the anode compartment. In order for this type of reaction to yield an acceptable cell e.m.f., the rate of attainment of equilibrium for the thermal reaction must be slow, as it is for the iodine-ferric ion reaction. But it is also necessary that a method be found to catalyze this thermal reaction in the dark electrode region. If this can be accomplished, then a cell will function in which the iodine-ferric ion reaction is displaced from equilibrium by light and is returned to equilibrium through the electrical circuit. The cell would then be a redox cell, in which Fe^{+3} is produced in the cathode compartment as part of an over-all photochemical process. At the anode compartment the Fe^{+3} would be formed at the electrode and would return to Fe^{++} thermally, that is, by oxidizing iodide. The current would be carried mostly by the I^- ion. Iodide would be formed photochemically in the light region and consumed in the dark.

The thermal oxidation of Fe^{++} by atomic iodine would appear to be an energy loss. However, as the ratio of (Fe^{+3}) to (Fe^{++}) builds up, the potential for the oxidation of Fe^{++} also increases, and in the limit

the $\text{Fe}^{++} \longrightarrow \text{Fe}^{+3}$ potential approaches that for $\text{I}^- \longrightarrow \text{I}_2$. The standard potential for the reaction

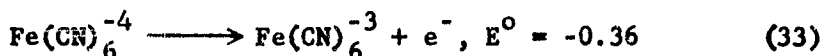


is calculated to be -1.30 v. Since the thermal oxidation of iodide by Fe^{+3} proceeds rapidly at room temperature it is remarkable that the production of Fe^{+3} can be observed in the presence of iodide. It has been postulated that either I_2^- or an activated I_3^- acts as an inhibitor for the thermal back reaction (Refs. 9 and 48).

An even more remarkable fact is the observation that while iodine (or I_3^-) in the presence of light oxidizes Fe(II) to Fe(III) against the gradient of chemical potential, in the presence of cyanide it reduces Fe(III) to Fe(II) , also against the gradient of chemical potential (Ref. 9). The three pertinent half cell reactions and their E° potentials are



and



Probably the photochemical system most extensively studied from the standpoint of a practical solar-photochemical converter is number 10, the photolysis of nitrosyl chloride. It appears attractive because the photolysis proceeds with perfect quantum efficiency at wavelengths at least as long as 6370 \AA and can theoretically be produced with a wavelength of 7605 \AA . Aside from practical difficulties associated with the making of a functioning photochemical converter, the maximum possible conversion efficiency is low because of the nature of the photochemical reaction mechanism.

The photolysis proceeds by the two steps



and



The primary process is endothermic to the extent of 37.78 kcal/mole, but the ensuing thermal reaction is exothermic by 19.72 kcal/mole. The result is that the net reaction is endothermic by only 18.06 kcal/mole

and the free energy change is only 4.86 kcal/mole at 25 degrees. A similar energy degradation occurs with number 3. This reaction is actually exothermic in the gas phase but the high energies of hydration of the hydronium and iodide ions make it endergonic in aqueous solution. Like reactions 5, 6, 10, 26, 27, and 28 it represents a possible two electrons per photon. Reactions 5 and 6 were listed in Table I as having measured quantum yields of only 1.0, but the difference is due to the convention adopted here of basing quantum yields on the absorbing species (except for the two reactions in which photosensitizers were used).

Reactions 18, 20 and 21 suffer from the same difficulty as 3 and 10; a considerable energy loss occurs as the result of a secondary thermal reaction. In these cases it is simply the recombination of halogen atoms. Number 19 is similar, but the energy loss is due to 1/4 of the bond energy of the oxygen molecule. In addition, all four reactions have the undesirability of having at least one solid phase. Mass transport in such systems becomes difficult, although some work towards making a working cell has been done (Ref. 49). These systems have the additional difficulty of needing organic dyes as photosensitizers in order to achieve a high fraction of their ultimate potential. Organic dyes themselves are generally light sensitive and somewhat unstable.

Finally, some mention should be made of reactions 29 and 30. Electron transfer spectra of these and many other chemical species have been reported (Refs. 50 and 51). It has been shown by Marcus how these might lead to solar energy conversion (Ref. 33). Number 29 was not included in the table since E_{max} was calculated to be less than one percent.

2.7 Maximum Current Density of a Photochemical Converter

A straightforward calculation can be made for the maximum current density of a photochemical converter in which the photochemical reaction occurs on or near the electrode surface. This maximum current density is a function of the solar quantum distribution curve and the threshold wavelength.

The total number of photons passing through one square centimeter per second is given by

$$n_t = \int_0^{\lambda_t} n(\lambda) d\lambda \quad (36)$$

where n_t is the total number of photons/sec/cm², λ_t is the threshold wavelength, and the function $n(\lambda)$ has been determined empirically (Ref. 2). Now the number of electrons per coulomb is

$$\frac{N}{F} = \frac{6.023 \times 10^{23}}{9.649 \times 10^4} = 6.245 \times 10^{18} \quad (37)$$

Therefore, one milliamp is 6.245×10^{15} electrons per second. The calculation has been made and is shown graphically in Fig. 2, in which threshold wavelength has been plotted against light flux on the left and current density on the right. The figure refers to conditions outside the atmosphere and one astronomical unit from the sun. It should be borne in mind that the current density plotted on the right refers to cases in which one photon gives rise to one electron. In many possible photochemical systems there would be two electrons per photon so that, obviously, the scale on the right would have to be doubled.

Since no photochemical reaction considered in this analysis has a threshold wavelength longer than 8030 Å, it can be seen from Fig. 2 that maximum electrochemical current densities will never be unreasonably high. The iodine-iron system described in Sec. 2.6 has a threshold wavelength of 8030 Å and would give a maximum of two electrons per photon. This implies a maximum current density of 72 milliamps/cm² for a steady state condition. Maximum power density in a steady state condition, which obviously corresponds to maximum efficiency, would come at a current density somewhat less than maximum possible current densities and would be determined in part by the design parameters of the particular converter in question, but more fundamentally by the kinetics of the electrode reactions and of the photochemical

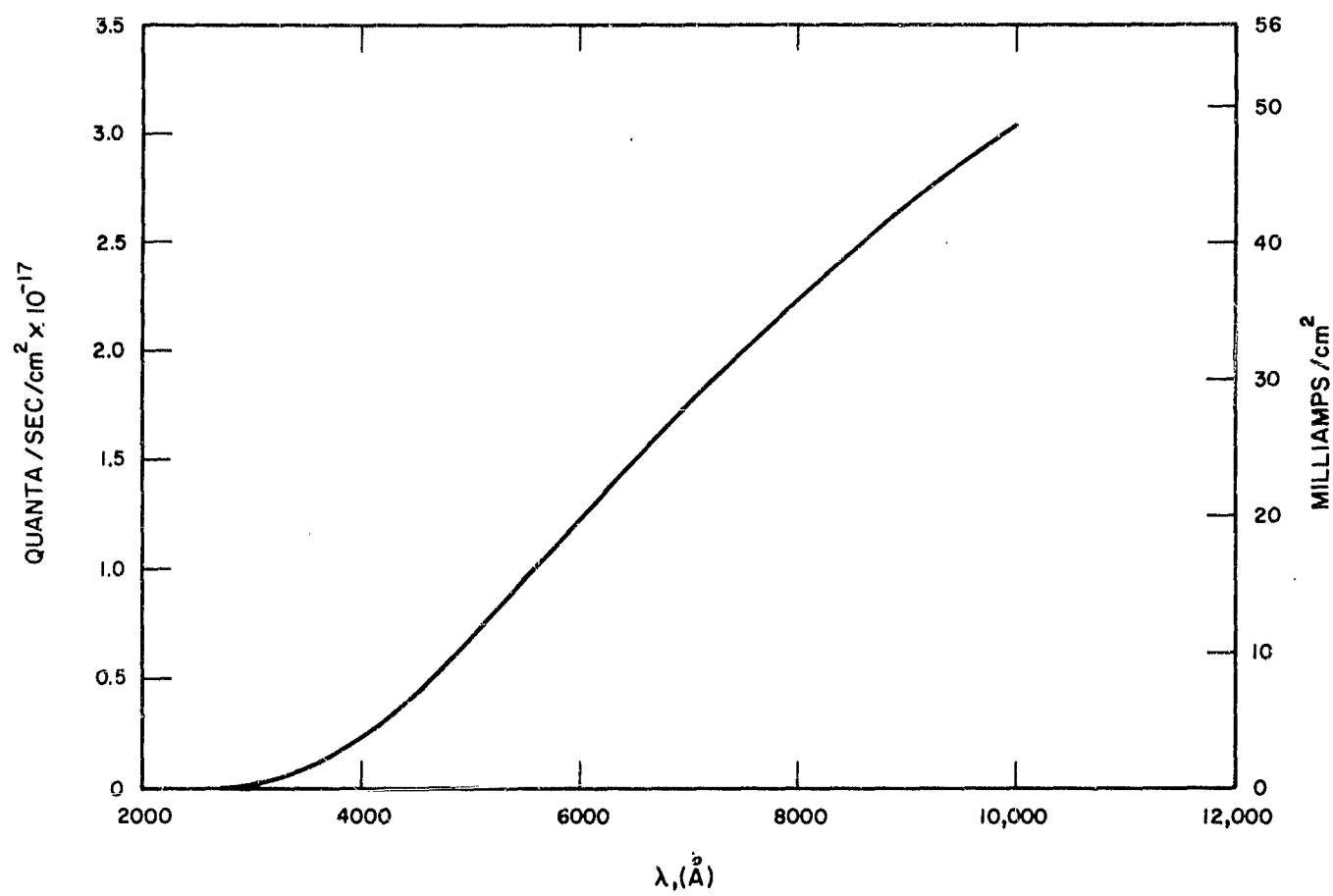


FIG. 2 MAXIMUM PHOTOCURRENT VS THRESHOLD WAVELENGTH

regeneration. Intuitively it can be seen that as the current density goes up, the concentrations of the reactants at the electrodes must go down and so must the cell potential. Since power is the product of cell potential and current there will be an optimum current density somewhere below the maximum as shown by Fig. 2 since that represents the maximum rate of photochemical regeneration. A more detailed analysis will require a knowledge of the kinetics of the photochemical step for each system as well as the kinetics of the electrochemical step.

3. THERMAL ENERGY CONVERSION

Thermal energy conversion is restricted in the following discussion to thermogalvanic systems. In principle, a vast number of chemical compounds can be used in a thermally regenerative fuel cell, but when specific compounds are considered, it is quickly realized that most of them would not be practical for one or more of several reasons. Since converter efficiency is in itself a very important criterion of the merit of any given conversion system, and since it has a very strong bearing on other important criteria (e.g., power/weight ratio), a brief discussion is given here of the theoretical conditions necessary for attaining Carnot efficiency in a thermally regenerative fuel cell. Special attention is also directed at some important properties of compounds which must be optimized in selecting those for use in these converters. A large number of compounds is then compared on the basis of some of these properties, and a short analysis of the kinetic aspects of a general thermally regenerative fuel cell system is given. Finally, the results of a very brief experiment program to evaluate one particular thermally regenerative fuel cell are given.

3.1 Conditions for Carnot Efficiency for Thermally Regenerative Fuel Cells

In the analysis of thermally regenerative fuel cells, done under Contract DA 36-039 SC 85270, the conclusion was reached that a condition for such systems to achieve Carnot efficiency was that $\Delta C_p = 0$. This conclusion was also reached by H.A. Liebhafsky (Ref. 52). More recently, however, J.B. Friauf performed a thermodynamic analysis of these cells and concluded that $\Delta C_p = 0$ was not the necessary condition but that Carnot efficiency could only be attained by the condition that $d(\theta\Delta H)/dT = 0$ (Ref. 53). A re-examination of our position, and that of Friauf, has led to the following conclusions.

The validity of Friauf's work is unquestionable, but there are some important special conditions under which $\Delta C_p = 0$ is also a valid

criterion. In discussing the conditions under which the efficiency of model 1, in EOS Report 420-Final, could be given by the relation

$$\eta = \frac{\Delta F}{\Delta H} = \frac{T_u - T_l}{T_u} \quad (38)$$

it was stipulated that the dissociation must take place reversibly at the upper temperature only. The effect of this condition on Friauf's criterion can be seen by considering the net heat input to the heat exchanger as given by Friauf. This heat is given by

$$d Q_n = \theta d\Delta H + \Delta H d\theta = d(\theta \Delta H) \quad (39)$$

"where θ is the degree of reaction, or the fraction of the road from zero to 100 percent product which the reaction has covered when equilibrium is reached" (Ref. 53). Now as the dissociation occurs at the upper temperature only, $d\theta = 0$ and $d(\theta \Delta H) = \theta d\Delta H$. But $d\Delta H = \Delta C_p dT$ and if $\Delta C_p = 0$, then $d\Delta H = 0$, and $d(\theta \Delta H)/dT = 0$. It can thus be seen that in the special case in which there is no dissociation except at the upper temperature Friauf's criterion can be reduced to $\Delta C_p = 0$.

It is now of importance to consider the practical implication of the conclusions just drawn. In EOS Report 420-Final it was brought out that three possible cases can lead to dissociation only at the upper temperature. For these cases $\Delta C_p = 0$ is a condition for Carnot efficiency. These cases are:

1. Two liquid phases and one gas phase present at the upper temperature.
2. Catalyst necessary for decomposition to occur at upper temperature.
3. Electrochemical decomposition at upper temperature.

Case 1 may prove to be very important since most chemicals for possible use in thermally regenerative fuel cells are metal salts, and metals generally are not soluble in their molten salts. Lithium hydride is an example of this. At the dissociation temperature there

exist two liquid phases and one gas phase. However, with this particular system an inert material must be added both because lithium hydride is a poor electrolyte and because its melting point is too high to allow an acceptable emf. Because of this, it can be shown that dissociation takes place continuously within the heat exchanger, so that $d\theta \neq 0$ and $\Delta C_p = 0$ cannot be a condition for Carnot efficiency. But an inspection of Table VI, p. 4-62 of EOS Report 420-Final, reveals that six compounds and their corresponding metals out of twelve in the table (ZnCl_2 , CdI_2 , GaI_3 , SnCl_2 , BiCl_3 , and TeCl_4) have melting points of 723°K (450°C) or lower. All of these compounds except possibly ZnCl_2 and GaI_3 are sufficiently good electrolytes that inert salts or salt mixtures (such as the quaternary halides used with lithium hydride) should not be necessary. Under these conditions $\Delta C_p = 0$ would be the criterion providing the dissociator temperature and pressure within the system are such that the metals and their salts are both liquid. The electrical conductivity data are reported by Kortüm and Bockris (Ref. 54).

It should also be pointed out in this connection that, in the general case, ΔC_p will usually be negative, where ΔC_p is defined as the heat capacity of the fuel cell product minus the heat capacity of the dissociator product. This arises from the fact that dissociation increases the number of species. This situation is fortuitous for thermally regenerative fuel cells in general, since a closer approach to Carnot efficiency is obtained than in cases for which $\Delta C_p > 0$.

As for case 2, an excellent example would be the dissociation of sulfur trioxide. If sulfur dioxide and oxygen are used as reactants in a fuel cell with a fused salt, metal sulfate eutectic, the product, sulfur trioxide, can be heated to a convenient temperature for decomposition. The decomposition rate is so low that sulfur trioxide does not, in fact, dissociate significantly except in the presence of a catalyst such as platinum. Again, $d\theta = 0$. Therefore, $\Delta C_p = 0$ is equivalent to $d(\theta\Delta H)/dT = 0$, although ΔC_p is not zero in this case.

Case 3 was discussed at some length in EOS Report 420-Final. A number of other investigators have also discussed it.¹ It is clear that in this case $d\theta = 0$ and that the condition $\Delta C_p = 0$ is equivalent to $d(\theta\Delta H)/dT = 0$.

The conclusion of this analysis is that Friauf's necessary condition for Carnot efficiency is always correct, but that it reduces in a number of important special cases to $\Delta C_p = 0$.

3.2 Further Remarks on Ideal Thermodynamic Efficiencies

In EOS Report 420-Final some ideal thermodynamic efficiency equations were derived. Two paradoxes which appeared in the analyses will now be clarified.

Figure 3 shows the ideal efficiency for a reversible cycle with $\Delta C_p = 0$. (The corrections for $\Delta C_p \neq 0$ were made in the earlier report). It was shown in the report that thermal dissociation can occur reversibly at the upper temperature only if a three phase system exists, leaving one degree of freedom. Thus, at the chosen upper temperature the dissociation pressure is fixed. Therefore, the pressure throughout the system is fixed, and no dissociation will take place until material reaches the upper temperature.

The following question has been asked: Since $\eta = \frac{T_2 - T_1}{T_2}$, how can efficiency also equal $\frac{\Delta F_{34}}{\Delta H_{34}}$ which contains low temperature functions only? The answer is that ΔF_{34} is not the standard free energy change, ΔF_{34}^0 , but is the free energy change at the existing concentrations, which are represented by the dissociation pressure, which is in turn determined by the upper temperature. Thus, ΔF_{34} is completely dependent on the upper temperature.

A second paradox can also be cleared up. Again, if $\Delta C_p = 0$, and only two phases exist, the dissociation can occur at the upper temperature only (e.g., by means of a catalyst), or dissociation can occur continually as MX is being heated up. These cycles can occur only if M and MX are completely miscible at the upper temperature.

1. Patent No. 2,635,431 by F.R. Bichowsky. See also footnote in Ref. 53.

Otherwise, there would be three phases, and the conditions for Model 1 in Fig. 3 would prevail. The efficiencies for a two phase system are now expressed by equations 40 and 41 based on Model 2 shown in Fig. 4. Equation 40 gives the efficiency in terms of the pressure of the gas X, and the equilibrium constants at the upper and lower temperatures. The paradox arises from the fact that station 4, the fuel cell outlet, contains nearly pure MX, and station 2, the dissociator outlet, is at the equilibrium expressed by K_u . Since these stations are defined, $\eta = \frac{\Delta F_{34}}{\Delta H_{34}}$ is fixed, regardless of dissociation occurring at all temperatures between T_u and T_l , or just at T_u .

An irreversible process, mixing, occurs (as discussed below) regardless of the dissociation occurring at T_u or between T_u and T_l . Therefore, the heat absorbed is determined by a state function and is independent of the dissociation path.

The relation $Q_p = \Delta H_p$ holds true only if no nonmechanical work is done as is the case from station 4 to station 3 via stations 1 and 2. Therefore, for the fuel cell $Q_p \neq \Delta H_p$, and therefore a net Q for the cycle can exist.

The three phase system arises from the existence of a non-ideal solution. If we assume the two phase solution to be ideal, then $\Delta F(\text{mixing}) = -\Delta TS(\text{mixing})$, since $\Delta H(\text{mixing}) = 0$. This assumption simplifies the following points, but is not a necessary assumption for the validity of Model 2. Consider the dissociation and mixing reaction:



Since the $\Delta F(\text{mixing})$ must be negative, the ΔF for the fuel cell is decreased, and thereby the efficiency for Model 2 is less than the efficiency for Model 1. Since the $\Delta S(\text{mixing})$ is positive, the $T\Delta S$ for the fuel cell is increased and since $T\Delta S$ for the fuel cell is negative, more heat is rejected in Model 2 than in Model 1.

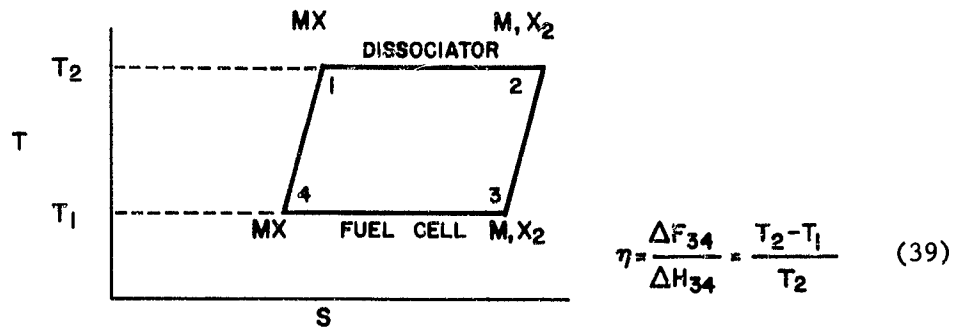


FIG. 3 MODEL 1

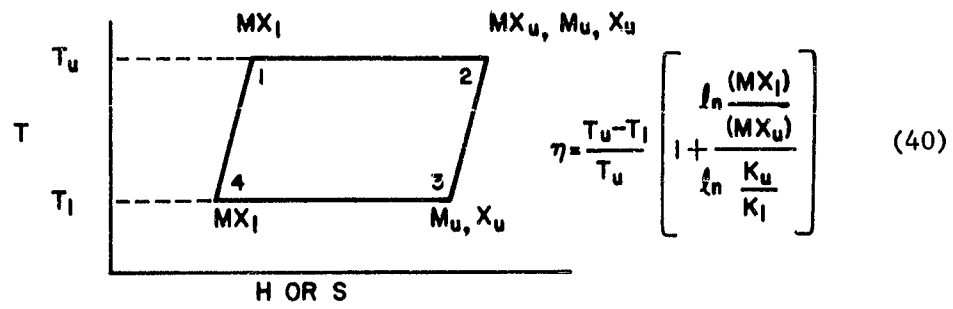


FIG. 4 MODEL 2

$$\eta = \frac{T_u - T_l}{T_u} \left(1 + \frac{\ln \left[\frac{1 + p^{1/2} K_u}{p^{1/2} K_u} \right]}{\ln \frac{K_u}{K_l}} \right) \quad (41)$$

3.3 Criteria for a Practical Thermally Regenerative Fuel Cell

Unfortunately there appears to be no single criterion by which to predict the most promising chemical system for a desired objective such as maximum efficiency or maximum power/weight ratio. It is quite clear that the ratio $\Delta F/\Delta H$ is not a useful property by which to predict either maximum efficiency or maximum power/weight. Its usefulness lies in its indicating, for a given chemical reaction and fuel cell temperature, the dissociation temperature for an ideal system in order to achieve Carnot efficiency. An ideal system in the sense used here is one in which there are no losses (e.g., direct thermal, electrical, heat exchanger, etc.) not inherent in the chemical net reactions. Its limited usefulness, even for this purpose, is apparent when it is realized that Carnot efficiency, even in theory, is possible for only a few reactions, e.g., those for which $d(\theta\Delta H)/dT = 0$. For a first approximation, reactions might be sought for which $d(\theta\Delta H)/dT$ is a minimum. To use this criterion alone, however, is to ignore the realities of other characteristics of actual chemical systems and of an operating cell. A set of criteria has been compiled which should prove useful in predicting one aspect of performance (i.e., efficiency). The set of criteria which follows was chosen to express the fact that there are thermal and electrical losses inherent in operating any real system, and that certain physical and chemical properties of a system might be of the greatest importance.

1. $|d(\theta\Delta H)/dT| \longrightarrow$ minimum
2. $\left(\frac{\partial E}{\partial T}\right)_P \longrightarrow$ maximum
3. $\sigma_{MX} \longrightarrow$ maximum
4. Minimum melting points and proper vapor pressure curves
5. Freedom from side reactions

The significance of $d(\theta\Delta H)/dT = 0$ has already been discussed. The importance of $(\partial E/\partial T)_p$ is that the cell emf is determined by this quantity. This quantity is equal to $\Delta S/nF$. The cell emf has a bearing on efficiency inasmuch as resistive losses in the fuel cell are equal to i^2R and power output is Ei . For a given power output the resistance loss within the cell will be smaller for a higher value of E . The value of σ_{MX} , the electrolyte conductivity, also has a bearing on efficiency through its effect on resistive losses and thermal losses. If an inert electrolyte has to be added because MX is itself a poor electrolyte, then more material will have to be transported and heat exchanger losses which are due to heat exchanger inefficiencies will be increased. The inert electrolyte will also add to the converter specific weight. Melting points should be as low as possible for all species since it is impractical to transport solids. Just what constitutes a proper vapor pressure curve for a given species will be determined mostly by certain chemical and physical facts about the particular system under consideration. The question of vapor pressure will be of most importance from the standpoint of separations. Probably the easiest way to affect separations is by phase difference. The final point needs no elaboration beyond saying that the entire system should be chemically stable indefinitely.

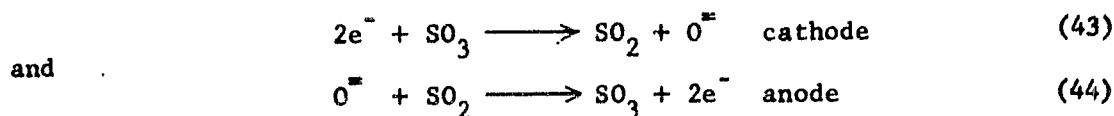
It can be seen by the tables in Sec. 3.4 that melting points and values of dE/dT vary over a wide range. Vapor pressures and electrical conductivities will also vary over quite wide limits but it is not evident how much variation is to be expected in $d(\theta\Delta H)/dT$, and it is certainly too early to assay the relative importance of these criteria.

3.4 Extension of Survey of Chemicals for Thermally Regenerative Fuel Cells

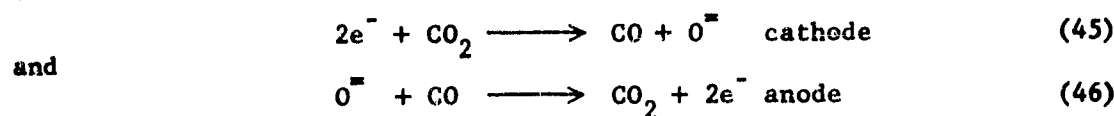
In EOS Report 420-Final some thermodynamic properties of a large number of inorganic compounds were compiled. They were all binary (two element) compounds in the initial study, since to include ternary or more complex compounds requires a preliminary study to determine the decomposition products of the dissociator. Except for inorganic ions in aqueous solution, no values of dE/dT were given in the previous report. Values of dE/dT (really $-\Delta S^0/n$) have been calculated for the binary compounds given in the previous report, in which only ΔH , ΔF , and $\Delta F/\Delta H$ were shown, and are compiled in Sec. 3.4.6 together with the melting points when available. In this report, the calculations have been extended to include ternary inorganic compounds and one class of organic compounds.

In the evaluation of these compounds for possible use in thermally regenerative fuel cells, the assumption was made that the systems would be anhydrous (except for two of the binary compounds) and that inert solvents or inert electrolytes would be absent. It would appear very difficult to evaporate water from a salt and then transport the salt to the dissociator.

It will be seen that many of the reactions represented by the compounds in the following tables are acid-base reactions. In order to operate an electrochemical cell, reactants must be capable of oxidation-reduction reactions. But the essential difference between the two types of reactions is that the former produce monomeric products and the latter do not. An electric current, therefore, cannot be directly produced from acid-base reactions but by the interposition of another compound, or "working gas" (as in the sulfuric acid concentration cell) a potential difference can be set up between two electrodes and a current can be drawn. For example, a decomposable metal sulfate could be used in a fused salt system with sulfur dioxide as a working gas according to the reactions



The thermal dissociation products of the salt MSO_4 would be MO and SO_3 . The SO_3 would have to be directed to the cathode where it would be reduced to SO_2 and leave free oxide ion. The compound MO would go to the anode where SO_2 is oxidized to SO_3 . The oxide ion disappears from the anode region. Similarly, the electrode reactions for the carbonate system would be



It must be borne in mind, however, that carbon monoxide disproportionates to CO_2 and carbon. The assumption is made here that at the fuel cell temperature the equilibrium would be well on the side of the monoxide.

For a large number of reactions of the ternary compounds it was necessary to estimate entropies in order to calculate free energies. These estimates were made by the method given by Latimer (Ref. 55). The thermodynamic quantities in all cases refer to the general reaction

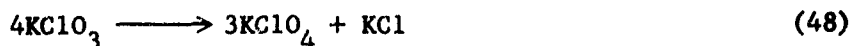


Only in the case of binary compounds are both A and B elements.

In the tables of this section, values of $-\Delta S^\circ/n$ are tabulated instead of dE/dT . The tabulated values differ, therefore, from ΔF only when n is different from one, and all values are positive numbers of convenient size to tabulate. But they are not quite dE/dT , which equals $-\Delta S^\circ/n\mathcal{F}$, where \mathcal{F} is the value of the Faraday. It should also be borne in mind that these values do not consider phase changes. If the compound in question undergoes a phase change between the fuel cell and dissociator then ΔF for the phase change can significantly effect $\Delta E/\Delta T$.

3.4.1 Oxy-Anions of the Halogens

Oxy-anions of the halogens generally will not be of much interest since they are usually high energy compounds. Even if they were stable at fuel cell temperatures their use for these purposes would be questionable, since their decompositions often involve disproportionation or yield more than one set of products. For example, KClO_3 decomposes as follows:

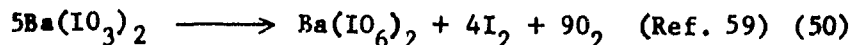


and to a lesser extent



The two reactions can take place simultaneously, and the process is complicated by the fact that KCl has an unpredictable but definite effect on the thermal decomposition (Refs. 56 and 57).

Potassium iodate is said to decompose to KI and O_2 and is therefore included in the table (Ref. 58). Calcium iodate decomposes to CaO , I_2 , and O_2 , and so was not included. Barium iodate decomposes as follows:



3.4.2 Oxy-Anions of Group VI

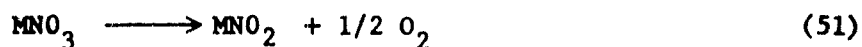
Enough definite information is available on the thermal decomposition of sulfates to include a number of them. Thus, PbSO_4 decomposes to PbO and SO_3 (Ref. 60). The sulfates of gallium, nickel, cobalt, cadmium, silver, and magnesium decompose to MO and SO_3 , but MnSO_4 is said to yield Mn_3O_4 , SO_3 and SO_2 and therefore was not included (Ref. 61). Gallium sulfate was not included due to insufficient thermodynamic data. The sulfates of bismuth (III), calcium, and copper (II) are also said to yield SO_3 and the corresponding oxides (Ref. 62).

No sulfites are included since it could not be shown that any of them decompose in a predictable way, such as yielding the metal oxide and SO_2 . Calcium sulfite yields CaSO_4 , CaO , and elemental sulfur (Ref. 63).

No thiosulfates were included since the thiosulfates of potassium, magnesium, sodium, ammonium, barium, and zinc give the sulfate and SO_2 (Ref. 64). Other sulfur species must also result, since sulfur (III) yields sulfur (IV) and sulfur (VI) in the decomposition and the oxidation state of the metal remains unchanged.

3.4.3 Oxy-Anions of Group V

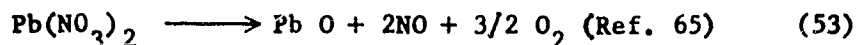
Alkali and alkaline earth metal nitrates decompose thermally according to



while the silver salt decomposes by



and the lead salt as follows:



Other oxy-anions of Group V elements do not appear to hold much promise for these purposes. The oxy-phosphorous compounds in general are quite complex and would not be expected to decompose reversibly. The oxides of the remaining three elements become progressively more basic and less volatile as the metallic character of the free element increases.

3.4.4 Oxy-Anions of Group IV

The only oxy-anions of importance here are the carbonates. The melting points of SiO_2 and of most silicates are so high as to preclude their use in fuel cells. Of the carbonates, direct evidence has been found only for the strontium and zinc salts that the decomposition products are really CO_2 and the metal oxides (Ref. 66); but for all others included, except the carbonates of the alkali metals, the oxides are stable at temperatures above the decomposition of the carbonates and so the products were presumed to be the metal oxides and CO_2 . This is not true of the alkali metal compounds, but they were included because the oxides, M_2O , might be formed on cooling

down to the fuel cell temperature. Certainly one of the oxides would be formed, and in the case of lithium it would certainly be Li_2O .

Oxalates were considered but they would be unsuitable since (at least with calcium) the carbonate is the initial decomposition product (Ref. 60). Oxalates would certainly not be regenerated in the fuel cell.

Cyanides of mercury, silver, and gold decompose thermally to give the metal and cyanogen (Ref. 67). Those of silver and mercury have been included but no data are available for the gold compound.

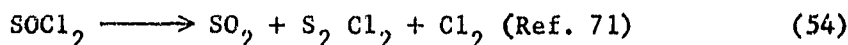
3.4.5 Borates

Since boron is the only non-metal in Group III, borates are the only members of the oxy-anions of Group III. There is very little thermodynamic information on these compounds, but judging from heats of formation, they are probably quite difficult to decompose.

3.4.6 Miscellaneous Inorganic Compounds

Several oxy-anions of the transition metals were looked at but none appear suitable as materials for thermally regenerative fuel cells. For example, CaCrO_4 yields many intermediate and complex compounds on decomposition, among which are $3 \text{ CaO} \cdot 6 \text{ CrO}_3 \cdot 2\text{Cr}_2\text{O}_3$ and $10 \text{ CaO} \cdot 6 \text{ CrO}_3 \cdot \text{Cr}_2\text{O}_3$ (Ref. 68). Silver permanganate gives Ag_2O , MnO_2 , and oxygen (Ref. 69). In general, the difficulty is that lower oxides of the transition metals tend to form, with the splitting off of oxygen, and there is no assurance that the original material can be regenerated in a fuel cell reaction.

Some additional compounds of interest have been considered. Sulfuryl chloride, SO_2Cl_2 , decomposes reversibly to SO_2 and chlorine (Ref. 70). Thionyl chloride was not included as it decomposes according to



Nitrosyl chloride decomposes to NO and the halogen (Ref. 72). Nitrosyl bromide is presumed to behave similarly.

There are some binary compounds which were not included in EOS Report 420-Final because they do not decompose to the elements. One is nitrogen dioxide (or nitrogen tetroxide) which can be decomposed as follows:



Another is sulfur trioxide, which decomposes in the presence of a catalyst as follows:



A third compound is carbon dioxide. Its decomposition might be represented by



but in view of the fact that the monoxide dismutates according to



it would be very difficult, if not impossible, to operate a thermally regenerative fuel cell based on the first reaction.

Finally, there is the compound cyanogen. This requires a special note of explanation. The compound dissociates thermally to cyanide radicals, but only at rather high temperatures (Ref. 73). The data on which the information in Table IV is based are from several sources. The enthalpy of formation is from Kistiakowsky and Gershinowitz, as are the entropies at 1500°K for both CN and C₂N₂ (Ref. 74). The entropy of C₂N₂ at 298°K is given in the "Handbook of Chemistry" (Ref. 66), and C_p was estimated from information given by Glasstone (Ref. 75). This allowed a calculation of the entropy of CN at 298°K from the relation

$$ds = C_p d\ln T \quad (59)$$

and, therefore, an estimate of the entropy and free energy of formation of C_2N_2 from CN radicals. This is another case in which it would appear very difficult to base a system on the reaction. It is not evident how the energy of the CN-CN bond might be realized.

3.4.7 Organic Hydrogenation Compounds

The thermal decomposition of many organic compounds is an irreversible process. One type of decomposition reaction which is reversible, however, is the catalytic dehydrogenation of certain organic compounds. Use has been made of this fact in designing a thermally regenerative fuel cell using these reactions (Ref. 76). The cell potential is due to a hydrogen partial pressure difference at two electrodes. This partial pressure is maintained high at one electrode by keeping the hydrogen in equilibrium with the dissociator. The other dissociator product is liquified, diverted from the hydrogen stream, and moved to the low pressure electrode. The hydrogen partial pressure is kept low at this electrode by maintaining the hydrogen in equilibrium with the compound being hydrogenated. The two electrodes are separated by an acid solution. Hydrogen goes into solution as the ion at one electrode, and is formed from the ion at the other. The net result is a method for making use of the free energy difference at the high and low temperatures while achieving a low cell resistance and good electrode characteristics.

In Table V, several possible compounds for use in this type of cell are examined in the same manner as the compounds in Tables III, IV, and VI. Table V refers to the reaction



at 298°K, where B is always hydrogen. Boiling points (in deg. K) were substituted for melting points as none of these compounds would be solid in any part of a fuel cell. All values in Table V refer to gases. This is only an approximation to the true condition since fuel cell reactant is a liquid at fuel cell temperature and pressure. It is

seen that the rate of change of free energy with temperature is somewhat lower with these compounds than with many of the inorganic compounds.

3.4.8 Inorganic Binary Compounds

Since cell emf is an important criterion for thermally regenerative fuel cells, dE/dT is an important property of a chemical system. Although the necessary thermodynamic data were compiled in EOS Report 420-Final for a large number of inorganic compounds, dE/dT was not calculated for them. Therefore, dE/dT (really $-\Delta S^0/n$) has now been calculated for them and compiled in Table VI, along with the appropriate melting points, in order that these compounds might be compared on the same basis with the ternary and organic compounds. Melting points are for AB and A, where AB refers to the compound, and A refers to the metal. When there is no metal involved, A refers to the higher melting point component. Melting points have been included because they have an obvious bearing on the selection of practical converters. When the melting point of a salt is too high, the solution usually is to dissolve the salt in a lower melting salt. This may be necessary anyway if the first salt has insufficient electrical conductivity. It will be noticed in Table VI that, in many cases, the metal has an extremely high melting point. This is undesirable because metals generally are not soluble in molten salts.

TABLE III
THERMODYNAMIC PROPERTIES OF TERNARY COMPOUNDS

Compounds	Dissociation Products	m.p. (AB)	m.p. (A)	ΔH_R°	ΔF_R°	$-\Delta S_R^\circ/n$	
GROUP VII							
KIO ₃	KI, O ₂	833	1000	-43.2	-24.7	10.4	
GROUP VI							
CoSO ₄	CoO, SO ₃	1153d	2073d	-58.8	-42.6	22.3	
NiSO ₄	NiO, SO ₃	1113d	2263	-60.1	-44.7	25.9	
CuSO ₄	CuO, SO ₃	>873d	1299d	-52.4	-39.3	22.2	
Ag ₂ SO ₄	Ag ₂ O, SO ₃	925	573d	-68.7	-56.1	21.2	
CdSO ₄	CdO, SO ₃	1273	1173d	-66.0	-53.7	20.7	
PbSO ₄	PbO, SO ₃	1443	1161	-72.6	-60.1	21.1	
Bi ₂ (SO ₄) ₃	Bi ₂ O ₃ , SO ₃	691d	1093	-375	-368	4.0	(1)
MgSO ₄	MgO, SO ₃	1458	3073	-67.2	-55.9	22.8	
CaSO ₄	CaO, SO ₃	1723	2845	-95.8	-82.7	22.6	
BaSO ₄	BaO, SO ₃	1853d	2200	-122.8	-108.6	23.2	
GROUP V							
LiNO ₃	LiNO ₂ , O ₂	534	—	-18.7	-12.6	10.3	(2)
NaNO ₃	NaNO ₂ , O ₂	581	544	-15.6	-9.0	11.0	(3)
KNO ₃	KNO ₂ , O ₂	616	570	-29.3	-23.4	9.8	(4)
Ca(NO ₃) ₂	Ca(NO ₂) ₂ , O ₂	834	—	-45.7	-33.2	10.5	(5)
Sr(NO ₃) ₂	Sr(NO ₂) ₂ , O ₂	843	—	-54.0	-40.9	11	(6)
Ba(NO ₃) ₂	Ba(NO ₂) ₂ , O ₂	865	490	-63.1	-50.6	10.5	(7)

- (1) Entropy estimated for Bi₂(SO₄)₃
 (2) Entropy estimated for LiNO₃ and LiNO₂
 (3) Entropy estimated for NaNO₂
 (4) Entropy estimated for KNO₂
 (5) Entropy estimated for Ca(NO₂)₂
 (6) Entropy estimated for Sr(NO₃)₂ and Sr(NO₂)₂
 (7) Entropy estimated for Ba(NO₂)₂

TABLE III (cont)

Compounds	Dissociation Products	m.p. (AB)	m.p. (A)	ΔH_R°	ΔF_R°	$-\Delta S_R^\circ/n$	
GROUP IV							
Li_2CO_3	$\text{Li}_2\text{O}, \text{CO}_2$	891	>2070	-54.1	-42.5	19.4	(8)
Na_2CO_3	$\text{Na}_2\text{O}, \text{CO}_2$	1124	sub	-76.9	-66.1	18.0	
K_2CO_3	$\text{K}_2\text{O}, \text{CO}_2$	1164	—	-93.5	-82.1	19.1	(9)
Rb_2CO_3	$\text{Rb}_2\text{O}, \text{CO}_2$	1110	673d	-96.7	-85.9	18.1	(10)
Cs_2CO_3	$\text{Cs}_2\text{O}, \text{CO}_2$	833d	633d	-97.5	-86.1	19.1	(11)
MgCO_3	MgO, CO_2	623d	3073	-28	-16	20.9	
CaCO_3	CaO, CO_2	1098d	2845	-42.6	-31.1	19.2	
SrCO_3	SrO, CO_2	1623d	2703	-56.1	-43.8	20.4	
BaCO_3	BaO, CO_2	sub.	2200	-63.9	-51.6	20.6	
MnCO_3	MnO, CO_2	d	1923	-27.9	-14.3	22.5	
FeCO_3	FeO, CO_2	d	1693	-21.0	-8.4	20.9	
CoCO_3	CoO, CO_2	d	2073d	-21.5	-10.1	19.8	(12)
NiCO_3	NiO, CO_2	d	2263	-12.1	-0.7	19.2	(13)
CuCO_3	CuO, CO_2	—	1299d	-11.1	+0.9	20	
Ag_2CO_3	$\text{Ag}_2\text{O}, \text{CO}_2$	491d	573d	-19.7	-7.6	20.1	
ZnCO_3	ZnO, CO_2	573d	>2070	-17.0	-4.4	20.9	
CdCO_3	CdO, CO_2	<773d	1173d	-23.8	-12.1	19.5	
PbCO_3	PbO, CO_2	588d	1161	-20.9	-10.1	18.0	
AgCN	$\text{Ag}, \text{C}_2\text{N}_2$	593	1234	-1.9	+3.8	19.1	
$\text{Hg}(\text{CN})_2$	$\text{Hg}, \text{C}_2\text{N}_2$	d	234	-11.1	+2.8	23.3	(14)

(8) Entropy estimated for Li_2O

(9) Entropy estimated for K_2CO_3 and K_2O

(10) Entropy estimated for Rb_2CO_3 and Rb_2O

(11) Entropy estimated for Cs_2CO_3 and Cs_2O

(12) Entropy estimated for CoCO_3

(13) Entropy estimated for NiCO_3

(14) Entropy estimated for $\text{Hg}(\text{CN})_2$

TABLE IV
THERMODYNAMIC PROPERTIES OF MISCELLANEOUS
INORGANIC COMPOUNDS

Compounds	Dissociation Products	m.p.(AB)	m.p.(A)	ΔH_R°	ΔF_R°	$-\Delta S_{R/n}^\circ$
C_2N_2	CN	246	—	-77	-68	18.9*
CO_2	CO, O_2	195(sub)	66/54	-67.6	-61.4	10.4
NO_2	NO, O_2	264	112/54	-13.5	-8.3	8.7
SO_3	SO_2 , O_2	290	198/54	-23.5	-16.7	11.3
NOBr	NO, Br_2	218	112/267	-2.04	-1.02	3.3
NOCl	NO, Cl_2	209	112/172	-9.03	-4.86	14.0
SO_2Cl_2	SO_2 , Cl_2	219	198/172	-22.0	-3	24.5

NOTE: m.p.'s are in degrees K, ΔH_R° and ΔF_R° are in kcal/mole,
and $-\Delta S_R^\circ$ is in cal/deg/mole.

* Entropy estimated for CN.

TABLE V

THERMODYNAMIC PROPERTIES OF SOME ORGANIC COMPOUNDS

<u>AB</u>	<u>A</u>	<u>b.p. (AB)</u>	<u>b.p. (A)</u>	<u>ΔH°_R</u>	<u>ΔF°_R</u>	<u>$-\Delta S^\circ_R/n$</u>
C_2H_6	C_2H_2	184	189	-74.43	-57.86	13.9
C_2H_6	C_2H_4	184	169	-32.74	-24.14	14.5
C_3H_8	C_3H_6	231	225	-29.70	-20.60	15.3
CH_3OH	$HCHO$	338	252	-20.4	-12.5	13.3
C_2H_5OH	CH_3CHO	351	293	-16.48	- 8.34	13.7
$n-C_3H_7OH$	C_2H_5CHO	369	323	-12.02	- 4.87	12.0
$i-C_3H_7OH$	$(CH_3)_2CO$	355	329	-10.62	- 1.70	15.0
C_6H_{12}	C_6H_6	354	353	-49.25	-22.96	14.7
C_2H_5OH	$CH_3COOC_2H_5$	351	350	-10.46	- 5.67	4.0
$C_2H_5NH_2$	CH_3CN	290	354	-32.6	-15.2	14.6

NOTE: m.p.'s are in degrees K, ΔH°_R and ΔF°_R are in kcal /mole,
and $-\Delta S^\circ_R$ is in cal/deg/mole.

TABLE VI SOME PROPERTIES OF BINARY COMPOUNDS

m.p.'s are in degrees Kelvin
 Sub means the compound sublimes
 $-\Delta S^\circ/n$ is in units of k cal/equivalent

Group I A				Group IV A			
	m.p.(AB)	m.p.(A)	$-\Delta S^\circ/n$		m.p.(AB)	m.p.(A)	$-\Delta S^\circ/n$
LiH	953	453	4.6	CCl ₄	250	>3925	3.5
NaH		371	4.6	C ₂ Cl ₆	460(sub)	>3925	4.4
KH		336	6.3	C ₆ Cl ₆	500	>3925	4.7
K ₂ O ₃	703	336	12.5	CBr ₄	322-63	>3925	2.7
K ₂ O ₄	>553	336	12.2	C ₂ Br ₆	421d	>3925	0.8
RbH		312	7.9	SiCl ₄	203	1693	4
CsH		301	2.8	SiI ₄	394	1693	4.9
Cs ₂ O ₄	873	301	15.8	Si ₂ I ₆	523	1693	4.7
Group II A				GeCl ₄	224	1232	4.2
BeBr ₂	763	1556	4.7	GeI ₂		1232	5
BeI ₂	783	1556	5.0	GeI ₄	417	1232	4.7
MgCl ₂	391d	923	3.2	SnCl ₂	519	505	5.7
CaH ₂		1123	4.6	SnCl ₄	240	505	4.2
SrH ₂		1043	4.6	SnBr ₄	304	505	5.2
BaH ₂		977	4.6	SnI ₂	593	505	5.0
Group III A				PbO	1161	600	3.5
BBr ₃	228	2313	3	PbO ₂	563d	600	3.5
BI ₃	316	2313	4	Pb ₃ O ₄	770d	600	5.6
BN	3270(sub)	2313	1.3	PbF ₄		600	11.0
AlBr ₃	371	933	4.7	PbCl ₂	774	600	5.5
AlI ₃	464	933	4.7	PbI ₂	675	600	5.2
AlN	2423 (at 4 atm)	933	2.6				
ScN		1673	2.5				

TABLE VI (cont)

Group V A

	m.p. (AB)	m.p. (A)	$-\Delta S^\circ/n$
NH ₃	195	63	4.3
PCl ₃	161	317*	3.8
PCl ₅	421	317*	6.1
PBr ₃	233	317*	4
PBr ₅	373	317*	6.2
PI ₃	234	317*	4.7
As ₂ O ₅	588d	631d	3.4
As ₄ O ₆	588	631d	3.2
AsCl ₃	255	631d	3.2
AsBr ₃	304	631d	4.3
AsI ₃	419	631d	4.7
Sb ₂ O ₃	929	904	6.5
Sb ₂ O ₄	1203d	904	3.4
Sb ₂ O ₅	653d	904	3.4
SbCl ₃	346	904	4.6
SbCl ₅	276	904	3.9
SbBr ₃	370	904	4.5
SbI ₃	440	904	4.7
Sb ₂ S ₃	823	904	0.7
BiO		544	3.2
Bi ₂ O ₃	1093	544	3.2
BiCl ₃	503	544	4.8
BiBr ₃	491	544	4.7
BiI ₃	712	544	5.2

Group VI A

H ₂ O	273	55	5.8
D ₂ O	277	55	6.1
H ₂ S	aq.		1.5

*Yellow phosphorous

Group VI A (cont)

	m.p. (AB)	m.p. (A)	$-\Delta S^\circ/n$
S ₂ Cl ₂	193	393	4.2
SCL ₂	195	393	3.5
SCl ₄	243	393	3.7
SeO ₂	613	490	3.4
SeCl ₄	578	490	4.8
TeBr ₄	653	725	5.0
PoO ₂			3.5

Group VII A

HF	aq.		8.3
HCl	aq.		8.6
ICl ₃	306	387	5.2
I ₂ O ₅	573d	387	3.6

Group I B

CuO	1299d	1356	3.3
Cu ₂ O	1508	1356	2.4
CuCl ₂	771	1356	5.0
CuBr	777	1356	4.0
CuBr ₂	771	1356	5.0
CuI	878	1356	4
Ag ₂ O	573d	1234	19.6
AgCl	728	1234	4.0
AgI	825d	1234	4.0
AuF		1336	4
AuCl ₂		1336	4.5
AuCl ₃	527	1336	4.7
AuBr ₃	433	1336	4.3

TABLE VI (cont)

<u>Group II B</u>				<u>Group IV B</u>			
	m.p. (AB)	m.p. (A)	$-\Delta S^\circ/n$		m.p. (AB)	m.p. (A)	$-\Delta S^\circ/n$
ZnCl ₂	556	693	5.5	TiH _{1.75}		2085	5.1
ZnI ₂	719	693	5.0	TiCl ₂		2085	9
CdO	1170d	594	3.5	TiI ₂		2085	5.5
CdCl ₂	841	594	5.5	TiI ₃		2085	5.3
CdI ₂	658	594	5.0	ZrBr ₄		2125	8
HgO	770d	234	4	ZrH _{1.5}		2125	5.7
HgCl		234	6.0	<u>Group V B</u>			
Hg ₂ Cl ₂	670(sub)	234	6.4	VCl ₃		2003	5.7
HgCl ₂	549	234	5.5	VI ₂		2003	5
HgBr		234	6	VBr ₃		2003	5.2
Hg ₂ Br ₂	618(sub)	234	3.3	VN	2323d	2003	2.1
HgBr ₂	509	234	2.6	<u>Group VI B</u>			
HgI		234	5.0	CrCl ₃	~1423	2178	5.5
HgI ₂	532	234	6.0	CrCl ₄		2178	3.7
<u>Group III B</u>				CrBr ₃		2178	5
GaBr		303	5	CrI ₂		2178	5
GaI		303	5	MoO ₃	1068	2890	3.1
GaI ₂		303	5.5	MoO ₄		2890	3.2
GaI ₃	485	303	5	MoCl ₂		2890	4.5
InI	624	430	6	MoCl ₃		2890	5
InI ₃	472	430	4.7	MoCl ₄		2890	4.7
Tl ₂ O	573	4.7		MoCl ₅	467	2890	5.5
TlCl ₃	298	575	5	MoCl ₆		2890	4.7
TlBr ₃		575	5	MoBr ₂		2890	4.5
				MoBr ₃		2890	5
				MoBr ₄		2890	4.7
				MoBr ₅		2890	4.6

TABLE VI (cont)

Group VI B (cont)			Group VIII (cont)		
	m.p. (AB)	m.p. (A)	$-\Delta S^{\circ}/n$		
MoI ₂		2890	5	NiCl ₂	1274 1723 5.2
MoI ₃		2890	5	NiBr ₂	1236 1723 5.5
MoI ₄		2890	5	NiI ₂	1070 1723 5
Mo ₂ N		2890	2.1	RuO ₂	2770 2.9
WCl ₂		3680	4.5	RuCl ₃	>770d 2770 4.7
WCl ₄		3680	4.7	RuBr ₃	2770 5
WCl ₅	521	3680	4.4	RhO	2233 2.8
WCl ₆	548	3680	3.8	Rh ₂ O ₃	~1400d 2233 3.0
WBr ₂	673d	3680	4.5	RhCl	2233 5
WBr ₄		3680	5	RhCl ₂	2233 5
WBr ₅	549	3680	4.6	RhCl ₃	~750d 2233 5
WBr ₆		3680	4.7	RhBr	2233 4
WI ₂		3680	5	RhBr ₂	2233 4.5
WI ₄		3680	5	RhBr ₃	2233 5
W ₂ N		3680	2	RhI	2233 4
Group VII B				RhI ₂	2233 5
MnI ₂	923	1517	5	RhI ₃	2233 5
MnCl ₃	353d	1517	5	PdO	1150d 1825 3.0
Group VIII				PdCl ₂	773d 1825 5
FeCl ₂	945	1808	4.6	PdBr ₂	1825 5
FeCl ₃	555	1808	12.9	PdI ₂	623d 1825 5
FeBr ₂		1808	5.0	OsCl ₂	2970 4.5
FeI ₂	865	1808	5	OsBr ₂	2970 4.5
CoO	2073d	1765	3.1	OsI ₂	2970 5
Co ₃ O ₄		1765	4.9	IrO ₂	2716 3
CoCl ₂		1765	5.1	IrCl	2716 4
CoBr ₂		1765	5	IrCl ₂	1046 2716 4.5
CoI ₂		1765	5	IrCl ₃	1036 2716 5.3
				IrBr	2716 4
				IrI	2716 3

TABLE VI (cont)

<u>Group VIII (cont)</u>				<u>Group VIII (cont)</u>			
	m.p. (AB)	m.p. (A)	$-\Delta S^{\circ}/n$		m.p. (AB)	m.p. (A)	$-\Delta S^{\circ}/n$
PtCl		2046	4	PtBr ₃		2046	5
PtCl ₂	854d	2046	5	PtBr ₄	453d	2046	5
PtCl ₃	708	2046	5.3	PtI ₂	598d	2046	5
PtCl ₄	543d	2046	5	PtI ₃		2046	5.3
PtBr		2046	4	PtI ₄	373d	2046	5.2
PtBr ₂	573d	2046	5				

3.5 Kinetic Considerations

In this approach to the kinetic analysis of thermally regenerative fuel cells an attempt is made to evaluate possible chemical systems in terms of their kinetic feasibility. This can be accomplished most advantageously by dividing the problem into two parts. One part concerns the kinetics of the regeneration step, and the other concerns the kinetics of the electrochemical step. In evaluating the first part an important criterion is the dissociator volume for a given cell current. The figure of merit might then be expressed in units of ma/cm^3 . The kinetics of the regeneration step is treated in Sec. 3.5.1.

Electrochemical aspects of fuel cells are evaluated as they apply to the present problem, with special reference to fused salt systems. The objective is to enable a first order estimate to be given for the electrochemical feasibility of a system in terms of known properties.

It is difficult to imagine that an analysis of this type could be definitive in the sense that any particular system might be absolutely dismissed on the basis of the analysis, but it might, instead, be quite useful as a method of screening. In the analysis of the dissociator kinetics, for example, it may turn out that the figure of merit for a given reaction is impossibly low, and yet methods for catalyzing the reaction may be feasible. The kinetic analysis might also be expected to indicate those systems in which some problems might arise with respect to reaction rates, as well as other systems which should be essentially free from these problems.

The analysis of this section is an extension of the kinetics analysis of the preceding contract, which was covered in EOS Report 420-Final. In that report the foundations were laid for estimating reaction rate constants based on activation energies for certain assumed mechanisms. Only the main features of the method will be discussed here.

3.5.1 Kinetics of Regeneration

First and second order reactions will be considered separately since the expression for the figure of merit is different in the two cases. Some justification for using gas phase kinetic expressions to evaluate condensed phase reactions will also be given.

3.5.1.1 First Order Reactions

For a chemical reaction in which n electrons take part, one ampere of current can result when $N/n\mathcal{F}$ molecules are reacting per second, where N is Avogadro's number, and \mathcal{F} is the value of the Faraday. Therefore,

$$1 \text{ ma} = 6.24 \times 10^{15} \left(\frac{1}{n}\right) \text{ molecules/sec.} \quad (61)$$

For a unimolecular, first order reaction

$$\frac{-d(AB)}{dt} = k_1 (AB) \quad (62)$$

where $-d(AB)/dt$ is the rate of disappearance of AB in the reaction



For one milliamp of current,

$$\frac{-d(AB)}{dt} = k_1 (AB) = 6.24 \times 10^{15} \left(\frac{1}{n}\right) \text{ molecules/sec/cm}^3 \quad (64)$$

if the standard state is one molecule/cm³. If the dissociator volume, in cm³, be denoted by V_D , then

$$k_1 (AB) V_D = 6.24 \times 10^{15} \left(\frac{1}{n}\right) \text{ molecules/sec.} \quad (65)$$

The factor (AB) can be expressed as

$$(AB) = \rho N X_{AB}/M.W. \quad (66)$$

where ρ is density in gm/cm³, N is Avogadro's number, X_{AB} is the mole fraction of AB , and $M.W.$ is its molecular weight. A figure of merit, θ_D , can now be defined as

$$\theta_D = \frac{1}{V_D} \quad (67)$$

and in the case of first order reactions

$$\theta_D = \theta_{D1} = \frac{k_1 (AB)n}{6.24 \times 10^{15}} = \frac{10^8 k_1 \rho n X_{AB}}{M.W.} \quad (68)$$

which has units of m^3/cm^3 . The constant in the numerator is not exactly 10^8 , but differs from it by less than five percent. This is sufficient accuracy since estimated values of k_1 will generally be accurate only to about an order of magnitude.

The figures of merit can be evaluated if the rate constants are known or can be estimated. A beginning of these estimations was made in the work reported in EOS Report 420-Final. A modification of the Arrhenius equation was used for first order reactions. The specific rate constant, k_1 , was related to the activation energy and temperature by

$$k_1 = \frac{kT}{h} e^{-E/RT} = 2.1 \times 10^{10} T e^{-E/RT} \quad (69)$$

which results upon simplifying the equation

$$k_1 = K \frac{kT}{h} \frac{Q^\ddagger}{Q} e^{-E/RT} \quad (\text{Ref. 77}) \quad (70)$$

In these equations k_1 is the first order rate constant, k is Boltzmann's constant, T is the temperature in degrees Kelvin, h is Plank's constant, E is the activation energy for the reaction, R is the gas constant, the Q 's represent total partition functions for the normal and activated species, and K is the "transmission probability" which is defined as the probability that an activated species will not be reflected back across the energy barrier during a reaction. This probability is generally assumed equal to unity. The partition functions are defined as the sum of the translation, vibration, and rotation functions, or,

$$Q = q_T + q_{\text{vib}} + q_{\text{rot}} \quad (71)$$

The Q^\ddagger function is exactly analogous but refers to the activated complex instead of the normal species. The first equation results from the second by assuming that $K = 1$, that the dimensions of the molecule are not changed by activation so that $q_{\text{rot}}^\ddagger = q_{\text{rot}}$, and that vibrations of complex and normal species are all high or identical so that $q_{\text{vib}}^\ddagger = q_{\text{vib}}$. The translational partition functions of the two species are also assumed equal.

In Electro-Optical Systems Report 420-Final it was pointed out that for a first order reaction, in the absence of a catalyst, the dissociation energy can be taken as the energy of breaking the A-B bond in the compound AB, or the BA-B bond in the compound AB₂, etc. This allows the θ criterion to be replaced by a criterion based on bond energies. A minimum order of magnitude for θ_D is about 10^3 . If $\rho = 2 \text{ gm/cm}^3$, a value of θ_D of 10^3 would imply a dissociator power/weight ratio of 0.15 watt/gm or 68 watts/lb. Thus the minimum dissociator material weight would be completely negligible if $\theta_D \geq 10^3$. If $n = 2$ (as it is for many reactions covered in the thermodynamics analyses), M.W. = 25 and $T = 1000^\circ\text{K}$, it can be seen from Eq. 73 that $E = 80.4 \text{ kcal/mole}$. For this type of reaction, bond energies in excess of 80.4 kcal/mole might lead to unacceptably low dissociator reaction rates.

If a pressure of 1 atm is used for gases and again a value of 10^3 for θ_{D1} is assumed, then by Eq. 76 the maximum bond energy is found to be 63.0 kcal/mole for a temperature of 1000°K .

It is of interest to consider the effects of the approximations made in the analysis thus far. The values of $\rho n/\text{M.W.}$ will almost always be within an order of magnitude of the value assumed here. The possible error introduced in assuming $X_{AB} = 1$ could be more serious than this, even if there is no inert solvent in the system. To assume $X_{AB} = 1$ is equivalent to assuming that the products of dissociation are withdrawn rapidly enough to make their concentrations negligible. The exponential factor in the rate constant varies one power of 10 for each 4.6 kcal/mole at 1000°K . In general, a reaction would be considered borderline only if the bond energy fell within about 5 kcal/mole of the value indicated.

For the gas phase reactions it is seen that θ_{D1} is directly proportional to the pressure, and it should be borne in mind that an extra 4.6 kcal/mole can be offset by a ten-fold pressure increase. In addition, all reactions are strongly temperature sensitive, and the more so the lower the activation energy. If the activation energy is 50 kcal/mole, then increasing the temperature from 1000 to 1100°K will increase the rate constant by about a factor of 10.

Care must be exercised in using Eq. 69 as it is valid for gases only in the limit of high pressure. The meaning of high pressure is given by Benson (Ref. 77). It can be seen that these pressures are a function of internal degrees of freedom, which, in turn, are partly determined by the number of atoms in the molecule. Table XI.2 of Ref. 77 shows that for molecules with four or more atoms, Eq. 72 would be valid at essentially any pressure encountered in thermo-galvanic converters.

The accuracy of the estimated specific rate constants should be borne in mind. The goal was to make any necessary simplifying assumptions which would allow rate constants to be estimated within about one order or magnitude. This does, in almost all cases, answer the question of feasibility, but rate constants of any systems showing borderline values of 0 would have to be evaluated experimentally.

Insertion of Eq. 69 into Eq. 68 gives

$$\theta_{D1} = \frac{2.1 \times 10^{18} \rho n T X_{AB} e^{-E/RT}}{M.W.} \quad (72)$$

Now if an average value of $\rho = 2$ and $X_{AB} = 1$ be assumed, the expression (72) reduces to

$$\theta_{D1} = \frac{4.2 \times 10^{18} n T e^{-E/RT}}{M.W.} \quad (73)$$

For the specific case of gases Eq. 73 can be further simplified. The gas density is given by

$$\rho = \frac{273 P M.W.}{22,400 T} \quad (74)$$

where P is pressure in atmospheres. This gives gm/cm³ for the units of ρ . When Eq. 74 is combined with Eq. 73 the relation reduces to

$$\theta_{D1} = 2.5 \times 10^{16} n P X_{AB} e^{-E/RT} \quad (75)$$

and if P is 1 atm. and X_{AB} is again set equal to unity (meaning a pure compound) then

$$\theta_{D1} = 2.5 \times 10^{16} n e^{-E/RT} \quad (76)$$

3.5.1.2 Second Order Reactions

For a bimolecular, second order reaction the rate equation becomes

$$\frac{-d(AB)}{dt} = k_2 (AB)^2 \quad (77)$$

Reactions for which a rate equation of the form

$$\frac{-d(AB)}{dt} = k_2 (AB) (C) \quad (78)$$

is required will not be considered at this time. Mechanisms leading to such expressions should very seldom be of importance, especially in the absence of an inert solvent. It was pointed out, however, in EOS Report 420-Final, that two different mechanisms may lead to an equation of the first type. Two molecules may approach side-to-side, or end-to-end. It is also stated in the above report that the dissociation of hydrogen iodide is the only reaction known to occur by the side-to-side mechanism. Therefore, in all other cases, an end-to-end mechanism will be assumed.

The figure of merit for bimolecular, second order reactions is given, then, by the relation

$$\theta_{D2} = \frac{1}{V_D} = \frac{k_2 (AB)^2 n}{6.24 \times 10^{15}} = \frac{6 \times 10^{31} k_2 n \rho^2 X_{AB}^2}{(M.W.)^2} \quad (79)$$

where k_2 is in units of $\text{cm}^3/\text{molecule}/\text{sec}$. Dividing by Avogadro's number yields

$$\theta_{D2} = \frac{10^8 k_2 n \rho^2 X_{AB}^2}{(M.W.)^2} \quad (80)$$

where k_2 now has units of $\text{cm}^3/\text{mole}/\text{sec}$.

Second order rate constants can be represented by the relation

$$k_2 = \bar{Z}'_{AB} P_T e^{-E/RT} \quad (\text{Ref. 7}) \quad (81)$$

where \bar{Z}'_{AB} is called the specific collision frequency and P_T is the steric factor as given by the transition-state theory. The factor \bar{Z}'_{AB} is given in terms of fundamental constants and atomic parameters as

$$\bar{Z}'_{AB} = \pi \sigma_{AB}^2 \left(\frac{8 kT}{\pi \mu} \right)^{1/2} \quad (82)$$

where σ is the collision diameter, k is Boltzmann's constant, T is absolute temperature and μ is the reduced mass which is given by

$$1/\mu = 1/m_1 + 1/m_2 \quad (83)$$

The factor \bar{Z}'_{AB} will almost never vary as much as an order of magnitude for the compounds of interest in this analysis if σ_{AB} is assumed equal to 3.5 Å and μ_{AB} is set at 50 atomic mass units. If these latter quantities are expressed in cm and gm respectively, Eq. 81 becomes

$$k_2 = 1.2 \times 10^{13} T^{1/2} P_T e^{-E/RT} \quad (84)$$

Combining Eq. 80 with Eq. 84 gives

$$\theta_{D2} = \frac{1.2 \times 10^{21} T^{1/2} P_T e^{-E/RT} n \rho^2 X_{AB}^2}{(M.W.)^2} \quad (85)$$

and if it be assumed that $\rho = 2$ and $X_{AB} = 1$ (i.e., a pure compound), then

$$\theta_{D2} = \frac{4.8 \times 10^{21} n T^{1/2} P_T e^{-E/RT}}{(M.W.)^2} \quad (86)$$

For the special case of gases ρ can again be expressed as in Eq. 74, and if again it be assumed that $P = 1$ atm and $X_{AB} = 1$, then Eq. 86 becomes

$$\theta_{D2} = 1.8 \times 10^{17} n T^{-3/2} P_T e^{-E/RT} \quad (87)$$

The θ criterion can be replaced by one based on bond energies as was done for first order reactions. Again n will be taken as 2,

M.W. = 25 and $T = 1000^{\circ}\text{K}$ will be assumed. Values of P_T are given by Benson (Ref. 77). If a value of 10^{-3} for P_T be used, then the maximum activation energy for a θ of 10^3 is calculated to be 66.2 kcal/mole. But it was shown in EOS Report 420-Final that for a bimolecular reaction (except for the decomposition of hydrogen iodide, which occurs in a slightly different manner) the activation energy is equal to about 30 percent of the bond energy for each bond broken. The decomposition of the molecule AB can be represented as follows, for a bimolecular reaction:



The species A may then combine to give A_2 or an atom abstraction reaction



may follow, but the activation energy for these atom abstraction reactions is known to be only about 5 percent of the bond energy of AB (Ref. 77) and should have no effect on the overall reaction rate. It can be seen from Eq. 88 that two A-B bonds are broken; therefore the activation energy should be about 60 percent of the A-B bond energy. Dividing 66.2 by 0.60 gives 110 kcal/mole for the maximum allowable bond energy for an uncatalyzed bimolecular reaction in a condensed phase.

For gas phase reactions a similar treatment yields 32.5 kcal/mole for the activation energy, implying a maximum bond energy of 54 kcal/mole.

The approximations made for second order reactions are similar to those for first order reactions, but ρ , X_{AB} , and M.W. each enters as the square instead of the first power. If θ_{D1} as given by Eq. 73 can be considered accurate to one order of magnitude, when making the simplifying assumptions necessary to apply it to general reactions, then θ_{D2} from Eq. 86 should, on the same basis, be accurate to within about two orders of magnitude. There is an

additional term in Eq. 86, however, which does not appear in Eq. 73. This is the steric factor, P_T , which could introduce an error of as much as two orders of magnitude by itself. For second order reactions, therefore, the θ criterion should be considered borderline unless the activation energy differs by more than about 18 kcal/mole from the maximum as given above. Under these circumstances, of course, the actual values of ρ , M.W., etc., and the estimated value of P_T (Ref. 77) should be used for the reaction in question.

3.5.1.3 Comparison Between Gas Phase and Condensed Phase Reactions

In the derivation of the rate constants it was assumed that the reactions were in the gas phase at unit activity. Many reactions of interest in this analysis will be in a condensed phase, even in the dissociator. The justification for this procedure is that reaction rates in the two situations are often very similar. Equation 70 can be put in the form

$$k_1 = \frac{kT}{h} \cdot \frac{Q^\ddagger}{Q_A Q_B} e^{-E/RT} \quad (90)$$

where the Q 's have the same meaning as before. The factor $(Q^\ddagger/Q_A Q_B) e^{-E/RT}$ is the constant for the equilibrium between the normal and activated species and can be represented by K^\ddagger . This constant can also be written

$$K^\ddagger = \frac{c^\ddagger}{c_A c_B} \quad (91)$$

where the c 's represent concentrations. More precisely, K^\ddagger should be given by

$$K^\ddagger = \frac{a^\ddagger}{a_A a_B} \cdot \frac{\alpha_A \alpha_B}{\alpha^\ddagger} \quad (92)$$

where the c 's have been replaced by a/α , the ratio of the activity to the activity coefficient. Now the rate constant can be given by

$$k_1 = \frac{kT}{h} K^\ddagger \frac{\alpha_A \alpha_B}{\alpha^\ddagger} \quad (93)$$

where K_o^\ddagger is the true equilibrium constant (Ref. 78).

The difference between gas phase and condensed phase reaction rates is due, therefore, to differences in the ratio $\alpha_A \alpha_B / \alpha^\ddagger$. The justification for omitting the α 's when considering gas phase reactions is that the condition of unit fugacity is often approached very closely. In a condensed phase, particularly in solutions, somewhat greater departures from ideality are often found. Qualitatively it can be said that such departures are associated with solute-solvent interactions. But from such measurements as have been made on the pertinent activity coefficients, reaction rate constants for bimolecular reactions in solutions should be only about 100 times those for the corresponding gas phase reactions, and for unimolecular reactions the rate constants should be about equal (Ref. 78).

3.5.2 Electrochemical Processes

A rather brief evaluation of the electrochemical aspects of thermally regenerative fuel cells will now be given, with special reference to fused salt systems.

It was pointed out in the dissociation kinetics analysis that the analysis could not be definitive since the possibility of catalysis was not considered. This is even more true for the electrochemical kinetics analysis inasmuch as catalysis of electrode reactions is intimately associated with normal electrode processes. That is to say, it may not be possible to carry out electrode processes in an "uncatalyzed" manner as was postulated for the dissociation reactions.

When considering electrochemical processes in a general way for cells in which energy is withdrawn from the system, four distinct steps may be recognized:

- a. Transport of the reactant to the electrode surface.
- b. Reduction (or oxidation) of reactant at the electrode.
- c. Ionic transport away from electrode region.
- d. Ion neutralization.

Slowness of step a results in concentration overvoltage, step b, in activation overvoltage, and step c in resistance overvoltage. It is doubtful that ion neutralization would ever be the slow step in a reaction, but if the situation did occur, then it would have an effect on concentration overvoltage. Equations describing each of these overvoltages in terms of current density, temperature, and other parameters will now be given.

3.5.2.1 Concentration Polarization

Whenever an electrochemical cell process takes place the electrodes become polarized, i.e., they are disturbed from their equilibrium condition. One source of this polarization is due to a difference in activity between the reactant at the electrode and the activity in the bulk of the solution in the electrode compartment.

This situation is termed concentration polarization and is expressed quantitatively by the relation .

$$\omega_c = \frac{RT}{n\mathcal{F}} \log_e \frac{i_l}{i_l - i} \quad (\text{Ref. 1}) \quad (94)$$

where

- ω_c is concentration polarization
- R is the gas constant
- n is the number of electrons per reaction
- T is absolute temperature
- \mathcal{F} is the value of the faraday
- i is current density
- i_l is the limiting current density.

This latter quantity, i_l , is in turn given by

$$i_l = \frac{Dn\mathcal{F}}{t\delta} a \quad (95)$$

where

- D is the diffusion coefficient.
- t is the total transference number of all ions except the ion being formed, e.g., at the anode of a fuel cell t would be the sum of the transference number of all anions present.
- δ is the thickness of the diffusion layer
- a is the activity of the reactant on the solution side of the diffusion layer

The diffusion coefficient is given by the relation

$$D = \frac{ART}{2} \quad (96)$$

where A is the equivalent conductance. Since specific conductance rather than equivalent conductance is the quantity usually tabulated, the diffusion coefficient can be given by

$$D = \frac{\sigma v RT}{2} \quad (97)$$

where A is the specific conductance and v is the volume (in cm³) of the solution containing 1 equivalent of solute. For thermally regenerative fuel cells this may, in some cases, also be the volume of solute. Combination of equations 95 and 97 yields

$$i_l = \frac{\sigma v RT n a}{t \delta} \quad (98)$$

Aside from the temperature and the two universal constants, the concentration polarization is given in terms of i, σ, v, n, d, t, and δ. It is now of interest to apply Eq. 94 to a typical fuel cell. Since most thermally regenerative fuel cells that have been considered would operate in fused salt systems, the estimates will be for them.

For a comparison, Fig. 5 is shown, where theoretical polarization curves are given for several assumed values of i_l (Ref.79).

In aqueous solutions, δ has been shown to average about 0.05 cm. (Ref.78). Kortüm and Bockris tabulate σ as a function of temperature for a large number of fused salts (Ref.54). Values range from about 5 x 10⁻⁷ to 20, but average about 1 ohm⁻¹ cm⁻¹ at typical fuel cell temperatures. If CdI₂ be taken for a specific example, it is seen that σ ≈ 0.19 ohm⁻¹ cm⁻¹ at 389°C. The volume of 1 equivalent is

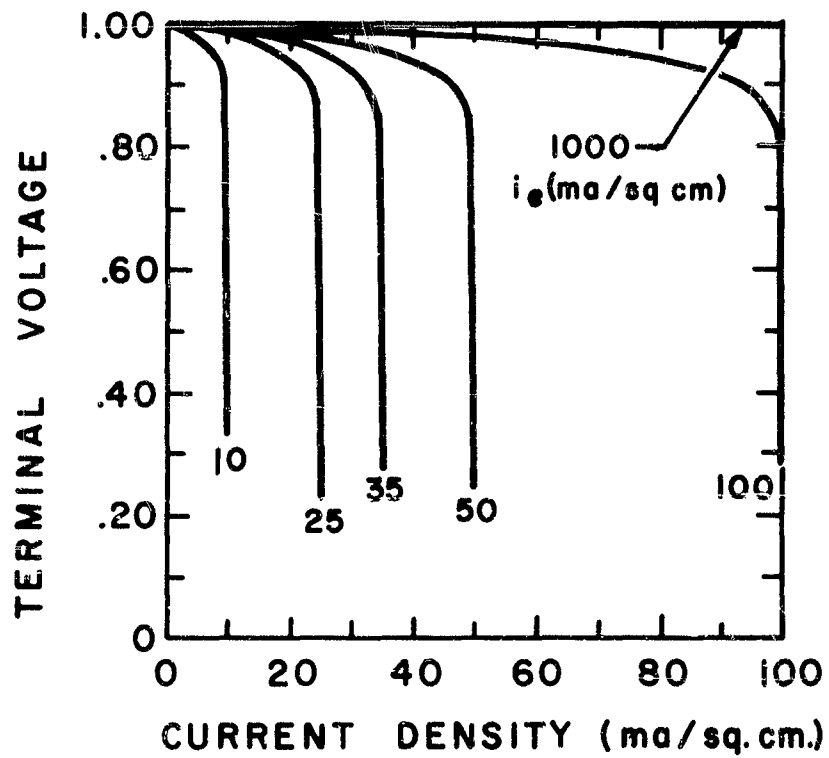


FIG. 5 CHARACTERISTIC PERFORMANCE OF CELLS
CONTAINING ONLY CONCENTRATION POLARIZATION

about 70 cm^3 . If it be assumed that $\delta = 0.05 \text{ cm}$, $t = 0.5$, and $a = 1$, it is seen by Eq.98 that the limiting current density is 73.4 amps/cm^2 . Concentration polarization is apparently no problem in most fused salt systems, providing unit activity of reactants can be maintained at the electrodes, and providing inert solvent-electrolytes are unnecessary. But for CdI_2 the upper temperature must be around 1600°C in order to maintain unit activity of reactants at 389°C , according to the analysis given in EOS Report 420-Final. Under some circumstances inert materials added to serve the function of solvent and/or electrolyte can lead to a lowering of the limiting current. It is evident from Eq.98 that the limiting current is proportional to the activity (approximately the concentration) of the reactant. This would be the case, for example, in the nitrate or carbonate systems where the compound MO_2 or MO might be dissolved in an inert material. In a system such as LiH , however, one reactant is a gas and the other a metal and neither would be dissolved in the inert electrolyte. Concentration polarization would be very serious in some systems in the absence of inert electrolytes. The compounds AlCl_3 , MoCl_5 , WCl_6 and probably HgCl_2 would have to be dissolved in an inert electrolyte in order to reduce concentration polarization to an acceptable level.

3.5.2.2 Activation Polarization

Electrode polarization caused by one or more slow steps in an electrode process is called activation polarization. In the absence of other polarization effects, the magnitude of the current density at a cathode is given by

$$i = i_o \left[e^{\alpha \mathcal{F} \omega_a / RT} - e^{-(1 - \alpha) \mathcal{F} \omega_a / RT} \right] \quad (\text{Ref.80}). \quad (99)$$

where i_o is given by

$$i_o = m k_1 a_+ e^{\alpha \mathcal{F} E / RT} \quad (100)$$

In these equations the symbols have the following meaning.

- α is the fraction of current in the forward direction
- ω_a is the activation polarization
- k_1 is the rate constant for the forward reaction
- a_+ is the activity of the reactant at the cathode
- E is the reversible electrode potential.

The constants R , T , n , and \mathcal{A} have their usual meanings, as given in Section 3.5.2.1. Eq. 99 can be solved for ω_a by observing that, except at very low current densities $e^{-(1-\alpha)\mathcal{A}\omega_a/RT}$ becomes negligible compared to $\alpha\mathcal{A}\omega_a/RT$. Therefore, it can be shown that

$$\omega_a = C + \frac{RT}{\alpha\mathcal{A}n} \log_e i \quad (101)$$

which, it will be recognized, has the form of the Tafel equation. The constant C is related to the other constants by

$$C = -\frac{RT}{\alpha\mathcal{A}n} \log_e i_o = -\frac{RT}{\alpha\mathcal{A}n} \log_e (\mathcal{A}k_1 a_+) - En \quad (102)$$

In order to use Eq. 101 for predicting the magnitude of the activation polarization for a cell in the absence of any experimental data α , k_1 , a_+ , n , and E will have to be known or estimated. It is usually assumed that $\alpha = 0.5$. The value of E , the reversible potential, is given by the thermodynamics of the system, as is a_+ . It remains to estimate k_1 .

The rate constant can be represented by

$$k_1 = B e^{-\Delta H^\ddagger/RT} \quad (103)$$

where B is a constant and ΔH^\ddagger is the energy of activation of the slow process responsible for the activation polarization. A reasonable approximation for the pre-exponential factor can be made but in the absence of any experimental data estimates for ΔH^\ddagger cannot be made at

this time. In the general case this activation energy is a function of the electrode material and physical state as well as the chemical system.

Figure 6 has been included to show the effect of activation polarization in the absence of other polarizations. The parameter, i_o , is sometimes called the exchange current (Ref. 80).

3.5.2.3 Resistance Polarization

A third polarization within a cell, sometimes called a pseudo polarization, is caused by electrolytic resistance. The magnitude of this polarization is given by

$$\omega_R = i\rho \frac{L}{A} \quad (104)$$

where ω_R is the resistance polarization

ρ is the specific resistance (or resistivity)

L is the distance between the electrodes

A is the electrode area.

It was pointed out in Section 3.5.2.1 that resistivities for fused salts are generally quite low. In some cases, e.g., LiH, it is necessary to add to inert electrolyte when the resistivity is too high. With LiH the inert solvent-electrolyte is also needed to lower the melting point of the system to allow an acceptable cell emf.

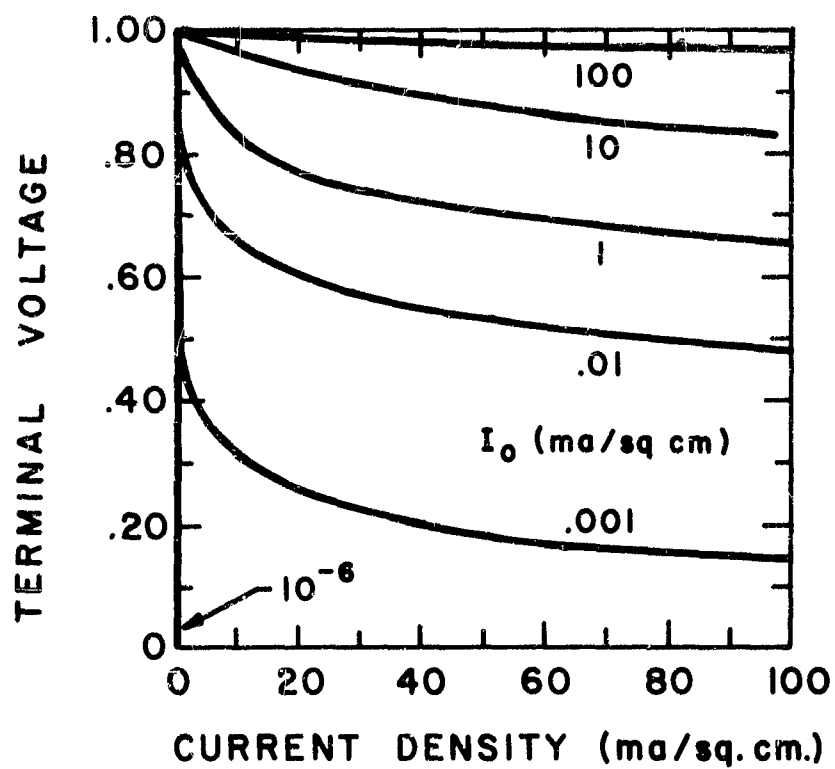


FIG. 6 CHARACTERISTIC PERFORMANCE OF CELLS
CONTAINING ONLY ACTIVATION POLARIZATION

3.6 Experiments with Sulfuric Acid Concentration Cell Converter

The results of the limited amount of experimental work are shown in Table VII in this section. The original plans were to conduct the experimental part in two phases. One phase was to have obtained experimental information on the electrochemical cell apart from the fractionator. The development of an efficient fractionator was to have made up the other half of the experimental program. It was further decided that fractionator designs could be best tested in connection with the electrolytic cells - that is, by building complete, working converters.

Separate electrolytic cells were never built but work was done on two complete units, one of which was completed and testing was just begun. An automatic control panel, metering, and recording unit was constructed for the purpose of getting completely automatic polarization curves as a function of temperature. This is described in Sec. 3.6.2.

3.6.1 Concentration Cell Designs

Work was begun on one cell which would have separated the function of the fractionator from that of the electrolytic cell. Figure 7 shows, in a semi-schematic way, the essential features of the design of this cell except for the manner in which the metal plates were to be fastened. The glass body of the cell had a wide, flat lip at top and bottom, and to these the plates were to have been clamped. A hollow metal O-ring would be used at the bottom, and a Teflon O-ring at top, for sealing.

The reasoning behind this design was that fractionation might occur rapidly up the center because the loose packing would offer much less resistance to gas flow than the tighter packing in the two annular rings. Also, more water would move up the center because of the larger cross section area. Sulfuric acid would react at the cathode and water at the anode and the products would return via the center column.

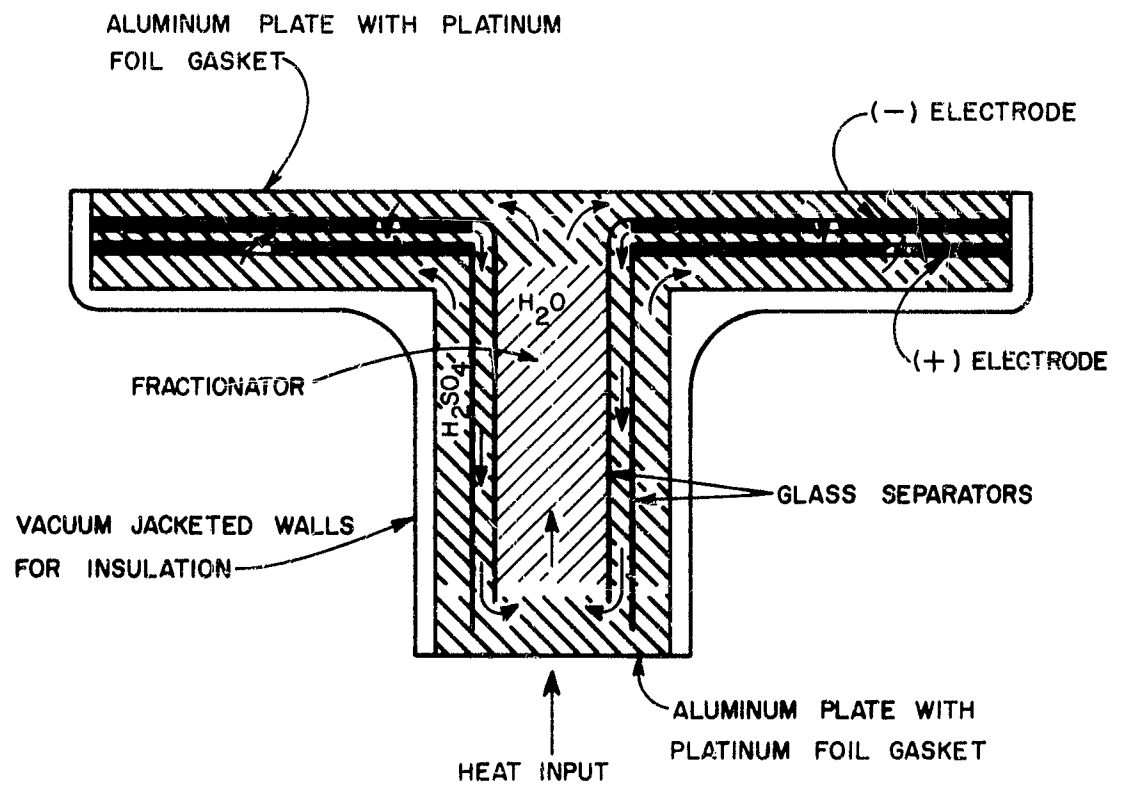


FIG. 7 CONCENTRATION CELL CONVERTER

It was expected that a pumping action would be set up as the result of the electrode processes. Thus at the dilute side water is consumed while H_3O^+ and oxygen are produced. The H_3O^+ moves into the region between the electrodes by conduction much more rapidly than HSO_4 moves in. The depletion would be made up by material from the back side of the electrode.

At the time the experimental program was stopped, the cell had not quite been completed because of some delay in getting delivery on all the necessary parts. It was decided that for the purpose of getting experimental data on electrode polarization, a cell similar to the one used on the previous Signal Corps program, Contract DA 36-039-SC-85270, could be made and testing could be started. However, this cell, shown in Fig. 8, differed in a few very important respects from the earlier ones as follows:

- a. It used porous tantalum of -200, +325 mesh and sintered. Platinum black was deposited on some electrodes. The electrodes used on the previous contract were sintered platinum of much bigger particle size.
- b. A 1/32" Teflon gasket was used at the top only, and the walls were stainless steel 0.010" thick. The bottom was brass 1/8" thick. On the previous model the walls consisted of the 3/16" Teflon O-ring between the top and bottom plates. By using Teflon only at the low temperature side, much higher temperatures could be used than previously.
- c. Holes were drilled into the brass plates to the center at both the high and low temperature sides, so for the first time really significant temperature readings were obtained. Both temperatures, and also the input voltage and current to the heater wire and output voltage and current were recorded simultaneously on one chart paper. This gave polarization curves automatically recorded for several high and low temperatures. The water flow rate was kept constant by means of a pressure reducer and micrometering valve. In order to prevent fluctuations in temperature, the cell was packed in glass wool and set in a Dewar flask.

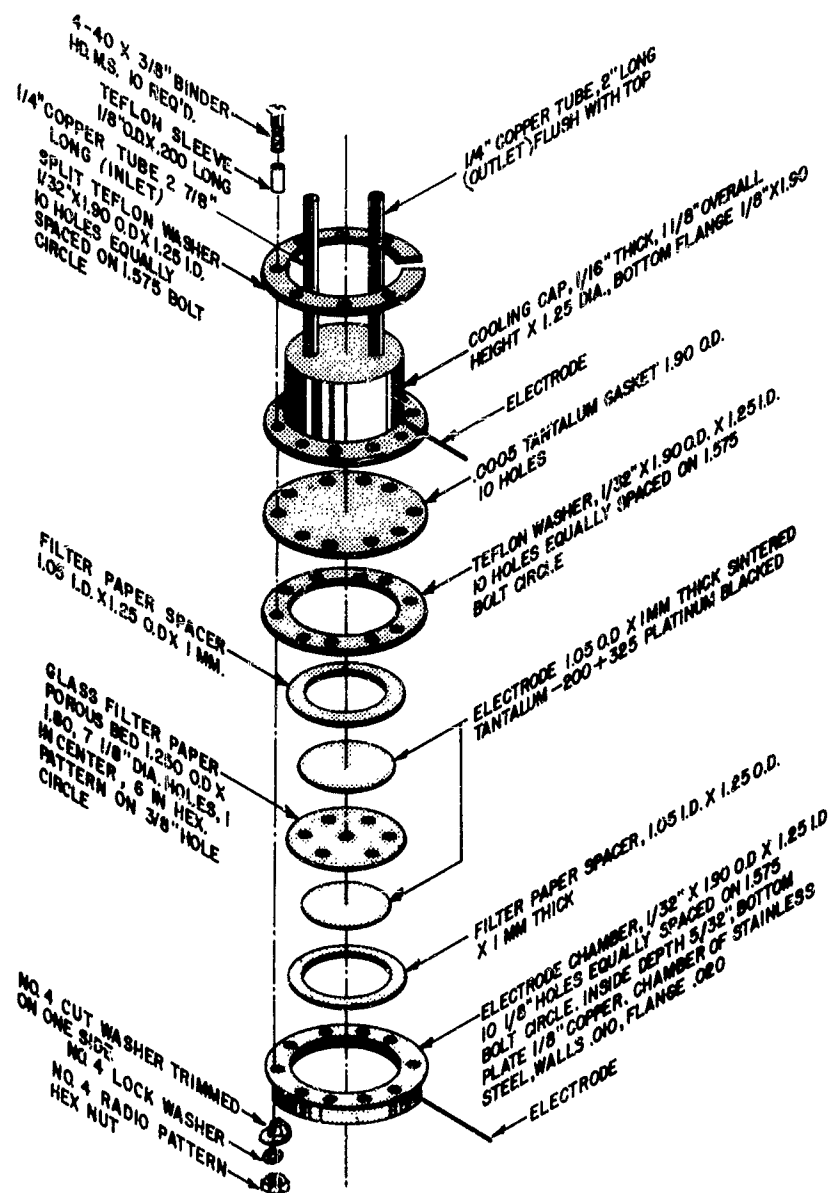


FIG. 8 CONCENTRATION CELL ASSEMBLY

3.6.2 Monitoring Circuit and Cycling Equipment

In order to control and monitor the heat input to the cell, it was decided to heat the unit electrically by means of a small Nichrome heater wire. The power was supplied by a battery eliminator in series with a lead-acid storage battery. The performance of the cell was followed automatically with a recorder which monitored the current and voltage of the cell, the current and voltage of the input to the heater wire, and the high and low temperatures of the cell. The controls went through one hour cycles automatically. The cell was heated for a half hour on open circuit. Then the resistance across the cell dropped continuously during the following half hour until it got to short circuit. It then returned to open circuit and remained there for the next half hour while the power to the heater advanced to the next position, and so on through ten cycles, at the end of which time the power to the heater was shut off. The monitoring circuit is shown in Fig. 9 and the circuit diagram for the cycling equipment in Fig. 10.

3.6.3 Performance

Very few data were obtained on the cell performance. The cycling and monitoring equipment functioned smoothly in the two runs which were made, but in the second run, immediately after the first polarization curve was obtained, the gold electroplate inside the cell failed. Since this occurred just before the change of direction of the program, the cell was never repaired. However, some interesting bits of information did come out of the two runs. Open circuit voltage is zero until the upper temperature is about 240°C . This is a little higher than previous measurements but it was noticed that all temperatures were somewhat higher than previously thought. This undoubtedly reflects the better position of the thermocouple wire. In the first experiment the open circuit voltage reached 0.55 at 352°C . No attempt was made to obtain polarization curves. Table VII shows the results of the second experiment.

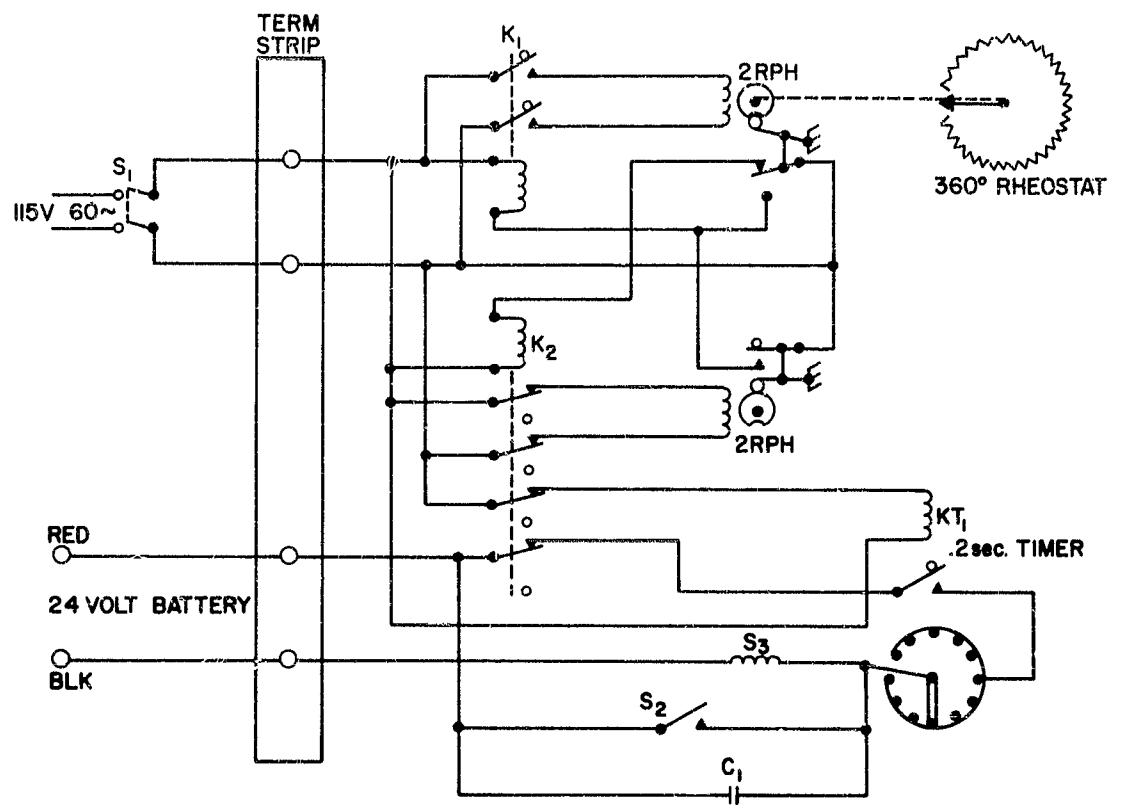


FIG. 9 MONITORING CIRCUIT

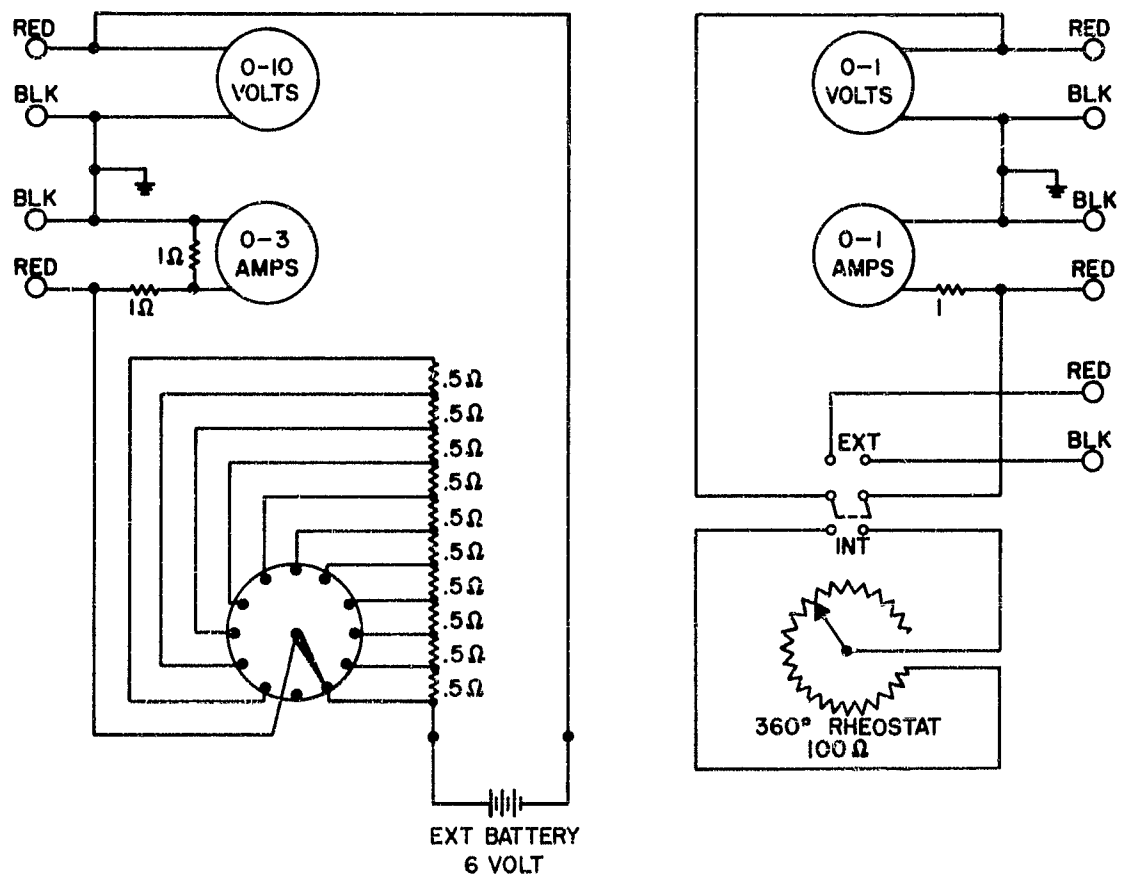


FIG. 10 CYCLING EQUIPMENT

TABLE VII
FIRST POLARIZATION CURVE FOR CONCENTRATION CELL

E_c	i_c	T_u	T_l	E_e	i_e
0.0	0.0	205	44	7.0	4.0
0.165	0.0	255	60	8.0	4.5
0.125	1.25	255	60	8.0	4.5
0.120	1.33	255	60	8.0	4.5
0.115	1.44	255	60	8.0	4.5
0.113	1.62	255	60	8.0	4.5
0.110	1.83	255	60	8.0	4.5
0.105	2.10	255	60	8.0	4.5
0.100	2.50	255	60	8.0	4.5
0.090	2.25	255	60	8.0	4.5
0.075	2.50	255	60	8.0	4.5
0.020	1.00	255	60	8.0	4.5
0.010	12.5	255	60	8.0	4.5

E_c = cell potential in volts

i_c = cell output current in milliamps

T_u = upper temperature in degrees centigrade

T_l = lower temperature in degrees centigrade

E_e = input voltage to heater wire in volts

i_e = input current to heater wire in amps

4. COMPARISON BETWEEN THERMALLY REGENERATIVE FUEL CELLS AND PHOTOCHEMICAL CONVERTERS

A comparison has been made between photochemical and thermal energy devices, where the thermal energy devices are mainly thermally regenerative fuel cells. Several of the points made are generally favorable to the thermal systems, while others are generally favorable to photochemical systems. The first four points in Sec. 4.1 are of such importance as to preclude the use of almost all known photochemical reactions.

It would be unrealistic not to make strong reference to space applications when considering photochemical systems. The reason is essentially that this is the area in which they will probably be better able to compete with thermal converters. It is brought out in the following discussion that energy conversion by quantum processes offers a method of operating at temperatures low enough to greatly minimize materials problems without paying a common penalty associated with low temperature thermal devices when operating in space-- that of low temperature heat rejection problems. It is not quite true that the Carnot limitation is not applicable, because thermal radiation from the sun is the prime source of power for photochemical reactions. But the limitation is not great since a perfect Carnot engine operating between 6000°K and 500°K would give 91.6 percent efficiency.

The radiation which is necessary for photochemical reactions can also be immediately degraded to heat and used in a thermal converter. Beginning with absorption, there are several steps involved with a photochemical-electrical converter, not all of which have an analog in thermally regenerative fuel cells, before the realization of an electric current.

4.1 Efficiency

There are several important criteria which might be used in comparing energy conversion devices. An interesting point about efficiency is that its importance lies in the extent to which it affects

other criteria, such as the power/weight ratio, power/volume ratio, cost, etc. But of any single criterion efficiency is generally the most important since the other criteria are almost always very strong functions of efficiency. This comparison will therefore begin with a rather detailed breakdown of factors affecting efficiency.

4.1.1 Light Absorption

One outstanding difference between the two systems is that the photochemical converter is invariably quite restricted in the wavelengths it can use and the thermal one is not. Many surfaces absorb almost completely throughout the ultraviolet and visible, but quite often begin to show very considerable reflectance in the near infrared. This is true of carbon black and platinum black. However, by making use of a cavity receiver, practically all radiation is absorbed. The degree of absorption is determined not by the wavelength of the incoming radiation, but by the temperature within the cavity receiver.

On the other hand, the material undergoing photolysis is usually a gas or a liquid whose absorption varies tremendously with wavelengths which are necessary for dissociation. Photocatalysts, species which absorb at the necessary wavelengths and can engage in energy transfer to the material to be photo-dissociated, are necessary and if the photocatalyst is not a solid, it is more than likely that a rather thick layer will be necessary for high absorption. In some cases, photochemical reactions can be sensitized on solid surfaces. Virtually complete absorption can then be achieved at all wavelengths useful for dissociation.

The mechanism of photosensitization by these solid surfaces, e.g., zinc oxide, cadmium sulfide, cadmium telluride, etc., is not well understood but appears to involve photoexcitation of electrons to a conduction band where they become available for reducing certain chemical species and the corresponding hole is available for oxidation. At least this is the mechanism postulated for hydrogen peroxide synthesis catalyzed on these surfaces. The formation of these electron-hole pairs is determined by the band-gap of the photocatalyst.

4.1.2 Quantum yield

Problems associated with quantum yields have no counterpart in thermal systems.

4.1.3 Activation Energy

Activation energy is more likely to be a problem with photochemical systems than with thermal systems. If a thermal dissociation process is slow, a catalyst can usually be found to bring about the reaction. On the other hand, for a photo-dissociation reaction, energy in excess of the bonding energy is usually necessary. This energy is degraded to heat. These effects are discussed in more detail in Sec. 2.1.

4.1.4 Back Reactions and Thermal Quenching Reactions

Many photochemical systems have an efficiency limitation as the result of thermal back reactions before product separation can be accomplished or before reaction can occur at the electrodes. After light absorption occurs the photo-excited species may undergo spontaneous fluorescence before dissociation is accomplished. There are no thermal analogs to these processes providing product separation is made at the highest temperature within the dissociator.

4.1.5 Thermal Energy Losses

Thermal converters of all kinds have problems of thermal energy losses. Direct heat transfer between the high and low temperature sides of a thermally regenerative fuel cell, may, with some designs, be a very important problem. Analyses previously have shown (EOS Report 420-Final) that with the simple thermocell and with the original design of the sulfuric acid concentration cell, direct thermal transfer alone can limit the maximum possible efficiency to a few tenths of a percent. Conduction, convection, and radiation may all contribute to this heat transfer. The transfer of heat through a photochemical cell is not a loss.

4.1.6 Effect of Heat Capacity Changes

Problems associated with ΔC_p do not exist with photochemical cells since the cell reactions are assumed isothermal and since heat is not the source of energy anyway. Heat exchangers are not needed and the design, at least in that respect, is simplified.

4.1.7 Non-Equilibrium Conditions

The attainment of equilibrium in the dissociator of a thermally regenerative fuel cell (at least at the highest temperature within the dissociator) is necessary for maximum efficiency. Non-equilibrium conditions within a photo-dissociator are necessary. Light energy is used to displace the system from equilibrium. Thermal dissociation, therefore, often requires a catalyst to maintain thermal equilibrium, while photo-dissociation often requires inhibitors to prevent thermal equilibrium from being attained.

4.1.8 Concerted Quantum Reactions

A concerted action of several quanta can initiate a photochemical process requiring energy beyond that of any of the individual quanta. This occurs in nature in the photosynthesis process, and in a modified form in the Hill reaction. Such a process evades the limitations imposed by Eq. 4 of Sec. 2.1, and in principle very high conversion efficiencies should be attainable by this method. But the photosynthesis process in nature (and the Hill reaction) are known to be quite inefficient. The efficiency of the photosynthesis reaction when converting sunlight is much less than one percent. (Ref. 81). It seems clear that what is really accomplished in nature is not the efficient conversion of solar energy, but the utilization of low energy quanta for a process so energetic that if carried out by a single quantum process the living cells would be killed. The photosynthesis process is endergonic to the extent of 112 kcal/mole, which corresponds to a wavelength of 2550 Å.

4.2 Versatility

Photochemical converters are less versatile than thermal converters in the sense that they will probably always be restricted to sunlight for the energy source, although it is conceivable they might be used in conjunction with a body heated to incandescence by some high temperature heat source. The materials problem associated with the latter possibility would be severe, since temperatures in the neighborhood of the melting point of any known substance would give an energy distribution curve shifted towards the red as compared to the solar curve. Photochemical reactions would then be needed which had especially low threshold energies. If the power is to be used in space missions the thermal systems would have the advantage of not being limited to the solar constant. This constant drops to a negligible value at the outer edge of the solar system.

Under special circumstances, it may even be advantageous to use more than one heat source for a thermal converter. If photochemical converters can only be used with sunlight, then this possibility is not open to them.

4.3 Thermal and Photochemical Energy Storage

For certain applications, such as low orbit satellites, it is necessary to store energy at times when the energy converter is not working. In principle, both thermally and photochemically regenerative fuel cells can store energy in themselves by storing reactants for the electrochemical cells. For thermally regenerative fuel cells the comparison has already been made (using the lithium-hydrogen cell as an example) between storage within the conversion device and storage in external fuel cells or batteries (Ref. 82). Another possibility is to store thermal energy as heat of fusion, heat of vaporization, heat of hydration, etc. This type of storage is not available to photochemical converters except possibly to a small extent by means of phosphorescent materials.

4.4 Effect of Light Concentration

Even low temperature thermally regenerative fuel cells need considerable light concentration in order to achieve acceptable collection efficiencies. Like photovoltaic cells, photochemical converters would function without light concentration - in fact, overall quantum yields generally decrease with increasing light intensity so that maximum efficiency should be reached with no concentration. Light concentration would undoubtedly result in higher temperatures, which in turn would increase thermal back reaction rates. In some systems the higher light flux would be a direct cause of increased deactivation by quenching and other reactions. In all probability the light concentration characteristics will more often be an advantage for the thermal systems. However, if photodissociation reactions can be found which can be made efficient even at slightly elevated temperatures, the photochemical systems might enjoy some very considerable advantages as will be pointed out in the next two sections. Such photochemical reactions might function at concentration ratios higher than the optimum for photovoltaic converters. For low orbit earth satellites the optimum concentration ratio for them is about 3:1 to 3-1/2:1. Since solar collectors are considerably lighter and less expensive than any photochemical or photovoltaic converters are likely to be, it would be desirable to have considerable light concentration.

4.5 Space Heat Rejection

Some thermally regenerative fuel cells, like the concentration cell converter being developed at Electro-Optical Systems, are low temperature devices. They have a very important advantage as compared to high temperature thermal converters from the standpoint of light collection efficiency, but sometimes heat rejection becomes a major problem. (However, it was indicated in Sec. 3.2 that it may be possible to design the converter so as to make the problem negligible.) It was pointed out earlier that photochemical reactions (also photovoltaic converters) have a threshold energy below which

the light is of insufficient energy to initiate the reaction. In most cases a very considerable fraction of incident solar radiation is of no value and can be reflected back into space. This greatly lowers the heat rejection problem while retaining the advantage of collection efficiency. It is the nature of a photochemical device, inasmuch as heat is not used, that heat rejection is accomplished at the same temperature as the light collection.

4.6 Materials Problem

As a consequence of low temperature operation, the materials problem would undoubtedly be considerably less than with thermally regenerative cells, especially those operating at 1000 to 1300°K at the upper end.

They should also be insensitive to harmful radiation if they are used with a light concentrator. One of the crucial questions about photochemical devices concerns the possibility of obtaining efficient operation at moderate temperatures -- temperatures high enough to allow considerable light concentration and relatively easy heat rejection but low enough for high efficiency of light collection and a very minimal materials problem.

5. COMPARISON BETWEEN THERMALLY REGENERATIVE FUEL CELLS AND OTHER THERMAL ENERGY CONVERTERS

A comparison has been made between two thermally regenerative fuel cells and a solar thermionic converter and the results are summarized in Table VIII. The lithium hydride cell was chosen because it is typical of a very large class of thermally regenerative fuel cells (where a metal salt dissociates to a metal and a non-metal) and because more developmental work has been done on it than on any other thermally regenerative fuel cell. The sulfuric acid concentration cell converter was chosen in part because it is a cell which we believe holds considerable promise, and one with which we at Electro-Optical Systems are very familiar, but also to contrast this low temperature system with two high temperature systems. The thermionic converter was the thermal system chosen to compare with the thermally regenerative fuel cells mostly for the reason that it has demonstrated the highest efficiencies, the lightest specific weight, and by far the highest power densities of any thermal-electric converter. In addition to the quantitative comparison between these three specific systems, some qualitative comparisons of a general nature are also briefly discussed.

In making the comparisons in Table VIII rather optimistic figures were chosen for the ultimate efficiencies to be expected from the two thermally regenerative fuel cells. To the best of our knowledge, no one has ever experimentally demonstrated high efficiencies from a thermally regenerative fuel cell in a closed system. The value for the sulfuric acid cell is in line with the theoretical estimate in EOS Report 420-Final. Laboratory model thermionic converters have already approached the 20 percent value listed in the table.

Figure 11 shows how sensitive collector efficiency is to the upper temperature, and therefore the advantage a low temperature converter has as compared to a high temperature one. At 2000°K the solar collector has to be better than a searchlight mirror, while at 670°K the worst mirror shown on the graph will give 90 percent collection efficiency. The values for collection efficiency for the two fuel cells are really the squares of the values assumed for the mirrors they would use. The reason is that it was assumed it would be advantageous to use a

TABLE VIII
COMPARISON OF THREE THERMAL-ELECTRIC
CONVERTERS

	<u>TRFC-LiH</u>	<u>THERMIONIC</u>	<u>TRFC</u> <u>H₂SO₄</u>
Upper Temperature, °K	1300	2000	670
Lower Temperature, °K	700	870	370
Converter Efficiency	0.15	0.20	0.15
Converter Wt., lb	267	11.3	55
Converter Specific Wt., lb/watt	0.53	0.023	0.11
Collector Efficiency	0.74	0.75	0.81
Collector Wt., lb	67.5	32.0	9.5
Collector Specific Wt., lb/watt	0.7	0.93	0.3
Weight of Auxiliary Equipment, lb.	96	0	0
Cell (or Diode) Voltage	0.5	1.0	0.5
Converter Voltage	4	8	28
Heat Rejector Wt., lb	2	3	2
Heat Rejector Specific Wt., lb/watt	0.004	0.006	0.004
Inverter Efficiency	0.36	0.75	—
Inverter Wt., Lb.	8	8	0
Total Wt., Lb.	441	54.3	66.5
Specific Wt., lb/watt	0.88	0.109	0.129

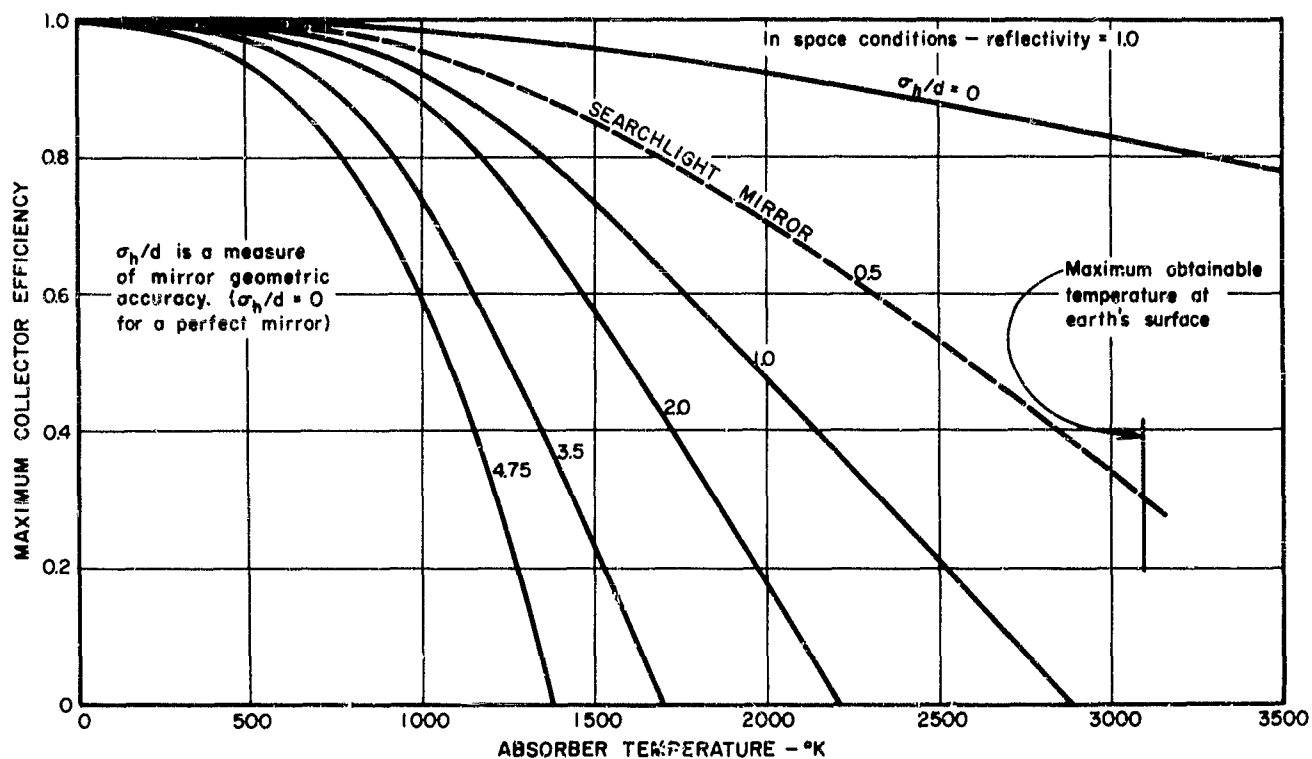


FIG. 11 MAXIMUM COLLECTOR EFFICIENCY VS ABSORBER TEMPERATURE FOR PARABOLIC MIRROR WITH RIM ANGLE = 60°

Cassagranian arrangement for these two converters. This means a second mirror, confocal with the collector mirror. Assuming that the overall efficiency for this two mirror system is the square of the efficiency for one mirror is only a rough approximation, but probably better than some of the other approximations which were necessarily made in this comparison.

It is difficult to overemphasize the advantage of a low temperature system with respect to light collection. Not only can collection efficiencies be greater, but this can be accomplished with much lower quality and therefore lighter weight mirrors. Mirror designs (including folding mirrors) are open to this type of system, which are not open to high temperature devices which must have high quality optics. Aiming accuracy is far less critical for a low temperature converter.

The process by which heat is rejected from a space power system is a critical design consideration. Thermionic, thermoelectric, and thermally regenerative fuel cell systems reject heat by direct conduction from the converter element to the radiating surface. Rankine cycle systems require a vapor-liquid condenser and radiator unit through which the working fluid circulates. A thermally regenerative fuel cell might use either a conduction radiator or a liquid radiator. The following considerations demand attention in radiator design and in the consideration of radiator characteristics as they affect system functions:

- a. Zero gravity condensation problems, which are important for Rankine cycle systems.
- b. Meteor puncture or leakage from fluid-containing systems which is important for fuel cells and Rankine cycle systems.
- c. Material selection - the radiator materials must have proper heat conduction characteristics but be compatible with other system materials. This is particularly critical for fuel cell and Rankine cycle working fluids.
- d. Radiator surface coatings to inhibit absorption of incident solar radiation. This is particularly important for low temperature, large-area radiators of the sort needed with turboelectric converters.

- e. Mechanical complexity involved with fluid-containing radiators, such as pumps, valves, and flow controls.

It may seem paradoxical that the really high temperature system, the thermionic, has a heavier heat rejector than even the very low temperature fuel cell. This is because, in principle at least, the thermally regenerative fuel cells can be built in the form of a hollow cylinder with the dissociator in the center. The thermionics need extra heat rejection because they operate at power densities of the order of 1000 times that of most thermally regenerative fuel cells. Heat rejection at 870°K is faster than at 370°K by a factor of only $(870/370)^4$ or 30.7. The figure for the heat rejector for the fuel cells is really for an aluminum radiation shield to shield the heat rejecting surfaces from the remainder of the satellite and to some extent from the earth.

The reason for the auxiliary equipment for the lithium hydride cell is to account for pumps, heat exchangers, separators, and controls. It is anticipated that none of these will be needed with the sulfuric acid cell, although a voltage regulator may be necessary.

It can be seen from Fig. 12 that the inverter efficiency is quite dependent upon the converter output voltage. In not having a metal reactant, as the lithium-hydrogen cell has the sulfuric acid cell should be capable of series connection to the point where the usual 28 volts dc can be attained without an inverter. Problems associated with metallic conduction between cells are quite severe with the lithium hydride converter. Thermionics are limited in this respect by heat losses in the wires connecting the cathodes and anodes. The effect on system weight is more than the weight of the inverter, as it also effects the size and weight of the solar concentrator.

It can be seen from Table VIII that the main advantage enjoyed by the thermionic converters is associated with their extremely high power densities which are reflected in a very low value of converter specific weight. If a better solution could be found for overcoming

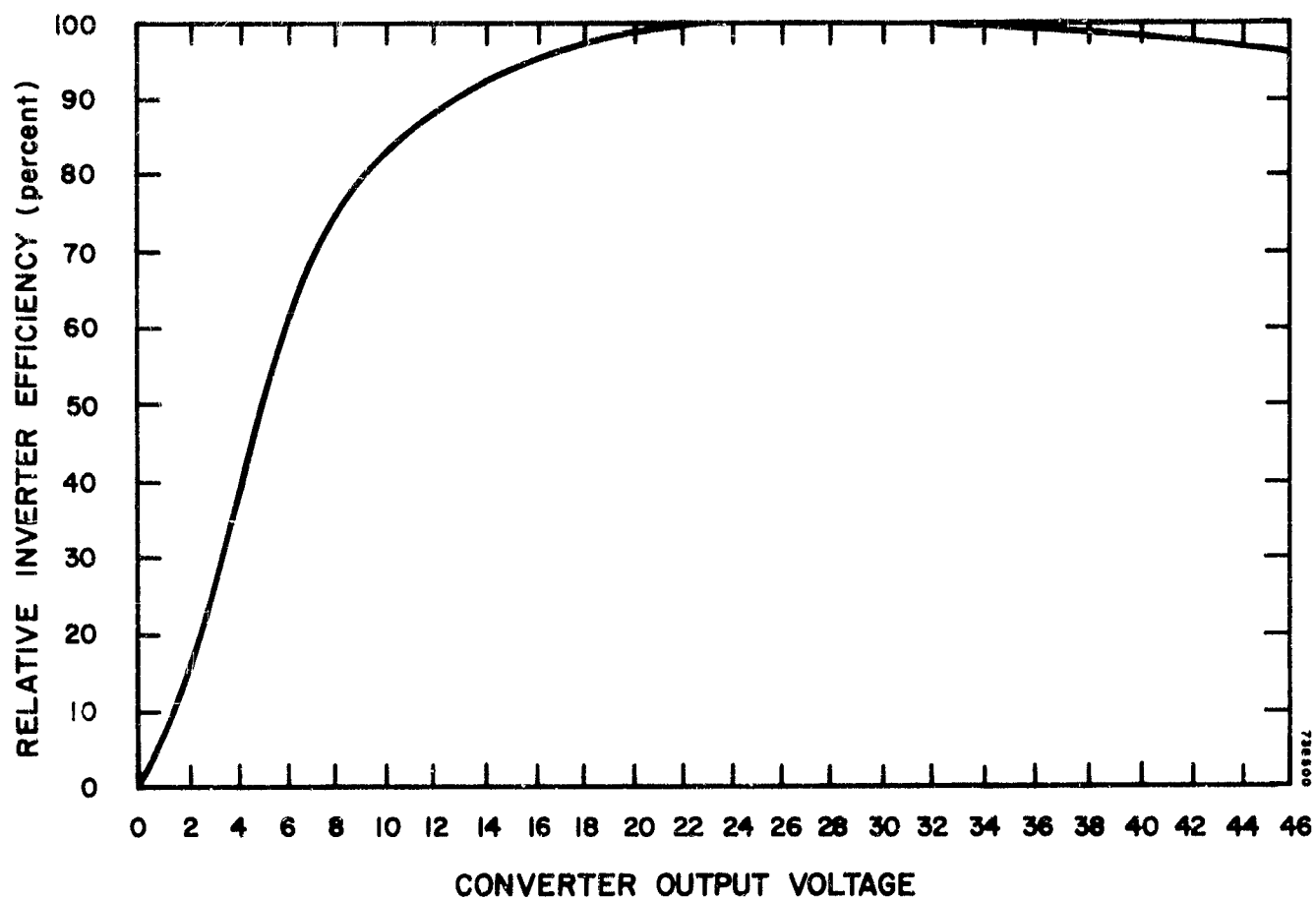


FIG. 12 INVERTER EFFICIENCY

activation polarization at an oxygen electrode in acid solution, it is expected that a somewhat lower figure for the converter specific weight for the sulfuric acid converter might result. The figure listed was based on power densities approximately equal to what have already been achieved.

For low altitude satellite orbits, energy storage requirements may be the controlling factor in system weight. The compatibility of various types of converters with energy storage devices is of paramount importance. In principle, all heat engines could utilize thermal storage, which in spite of converter inefficiency generally results in a lighter system than one using electrochemical storage. Unfortunately, however, suitable thermal storage materials are not available for all temperatures. The best thermal storage material, lithium hydride, is suitable only for systems having a maximum cycle temperature below 950°K . Some moderately suitable materials are available for temperatures up to 1250°K , but no materials are yet available for systems operating at temperatures of 2000°K . Therefore, thermionic systems and some thermally regenerative fuel cells must rely on electrochemical storage with its inevitable weight penalty. However, the thermally regenerative fuel cell presents a possibility of incorporating the storage function integrally with the cell, at some weight savings.

Output voltage is a basic parameter which is frequently overlooked when comparing electric power systems. Several of the systems being considered, fuel cells in particular, produce inherently low voltages per converter unit. This low voltage power cannot be used efficiently and must be raised to a higher voltage by inverters or by connecting converter units in series. A typical spacecraft requirement is that the power system produce 28 volts dc. The lower the converter output voltage, the more difficult it is to achieve the 28 volt goal. Connecting the converter units in series involves reliability problems. Furthermore, some types of converters do not lend themselves to multiplicity or to series connections. For example, thermionic converters are more efficient in large sizes because of the difficulty of preventing

heat losses when using many small diodes. Some thermally regenerative fuel cells, (e.g., the lithium hydride cell) may be even more difficult to series-connect because of the necessity of electrically isolating the electrolyte for each cell. The presence of a metal reactant is even more serious. It does not seem reasonable to consider building a large number of small, complete fuel cell systems including individual regenerators, separators, pumps, controls, and heat exchangers. Electrical isolation of the cells can be accomplished, but not always without difficulty. The use of inverters does not offer a penalty-free alternative to series connecting, because inverter efficiency depends strongly on input voltage as mentioned earlier. It can be seen that fractional-volt converter output is unacceptable. Therefore, even when using inverters, some series connection is required to achieve a suitable inverter input voltage.

One very important consideration in long range planning is the present state-of-the-art in relation to theoretical expectations. Rankine cycle systems are now performing within a few percent of their theoretical capabilities. Thermoelectric and thermionic systems are reasonably well developed but still far from the theoretical maximum. Demonstrated performance in thermally regenerative systems is orders of magnitude below theoretical maximum, but sound estimates, using present day knowledge, indicate that vastly better performance could be expected almost immediately. Actually, some further work must be accomplished before performance limits can be clearly defined.

6. CONCLUSIONS

Some conclusions concerning photochemical energy conversion are immediately evident. Endothermic reactions with threshold wavelengths long enough to allow acceptable efficiencies are rare. Of the ones which are known, in most cases either good quantum efficiencies have not been realized or a considerable fraction of the energy conversion is wasted in thermal degradation reactions. However, reactions based on iodine appear to hold a good deal of promise as the threshold wavelength is near the optimum for solar energy conversion; also two photochemical reactions of iodine have been studied which have no inherent thermal degradation reactions associated with them and which have given essentially perfect quantum efficiencies at all wavelengths studied.

Conclusions concerning thermal energy conversion with thermally regenerative fuel cells are somewhat less definitive. One reason is that, unlike the photochemical reactions, there are very many reactions known which can, in principle, be used in these cells and there appear to be more criteria which must be considered in selecting the best systems. Five criteria have been proposed by which chemical systems might be compared. The ultimate efficiency limit is set by the value of $d(\Delta H)/dT$. Friauf has shown that this quantity must be zero at all temperatures between the fuel cell and dissociator in order for Carnot efficiency to be realized. This is a necessary, but certainly not sufficient, condition for Carnot efficiency and, in practice, some of the other criteria may prove to be more important in the sense that it may be more difficult to find reactions which meet those criteria well enough. Thus, many reactions look unattractive because of undesirable side reactions, insufficiently high electrolytic conductivity, melting points which are too high, or because the rate of change of emf with temperature is too low. This latter property has not

been completely evaluated in this report for all reactions, since free energy changes associated with phase changes have not been considered. But in the absence of this latter effect, it would seem that most reactions suffer from a rather low value of dE/dT , or rate of change of potential with temperature.

Any comparison between thermally regenerative fuel cells and other thermal energy converters is somewhat speculative at this time, but from information (and lack of information) available at this time it appears that the sulfuric acid concentration cell converter should ultimately prove to be a very strong competitor to other systems.

7. OVERALL CONCLUSIONS

Although no thermally regenerative fuel cell nor photochemical converter has yet been brought to the threshold of practicability, for some systems there appear to be no theoretical limitations preventing their practical development. In particular, it appears that the photodissociation of iodine offers a method for converting sunlight which would likely prove to be far less expensive than photovoltaic converters. Some thermally regenerative fuel cells, such as the concentration cell converter, offer the possibility of low cost, low temperature thermal energy conversion which should prove to be highly competitive for a number of applications.

8. RECOMMENDATIONS

An effort should definitely be made to experimentally evaluate the photodissociation of iodine from the standpoint of energy conversion, as the present analysis indicates it is potentially capable of converting sunlight with almost 40 percent efficiency. A number of different methods for realizing this possibility should be looked at in addition to the one outlined in this report.

Since for the thermochemical systems the theoretical possibility exists for their being used as the basis for practical energy conversion devices in some cases and since some of them should offer several very attractive characteristics as compared to other energy converters, considerable effort should be exerted in this field. The chemical and thermodynamic characteristics are apparently suitable in some cases, but a major effort needs to be made in connection with the mechanical designs. In fact, it would seem that some radical new design concepts are necessary in order to achieve success in this field.

9. IDENTIFICATION OF KEY TECHNICAL PERSONNEL

Mr. J.J. Rowlette, Project Supervisor, and Mr. F.A. Ludwig, Scientist, were the only key technical personnel working on this contract. Following are the total labor hours expended by them:

Rowlette: 1916 hours

Ludwig: 164 hours

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